Ecotoxicology and Environmental Safety 149 (2018) 257–266

Contents lists available at ScienceDirect

Ecotoxicology and Environmental Safety

journal homepage: www.elsevier.com/locate/ecoenv

Review

Removal of emerging pharmaceutical contaminants by adsorption in a fixed-bed column: A review

M.J. Ahmed[b,*], B.H. Hameed[a]

[a] School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia
[b] Department of Chemical Engineering, Engineering College, University of Baghdad, P.O. Box 47024, Aljadria, Baghdad, Iraq

ARTICLE INFO

Keywords:
Pharmaceuticals
Adsorption
Fixed bed
Breakthrough curves
Modeling

ABSTRACT

Pharmaceutical pollutants substantially affect the environment; thus, their treatments have been the focus of many studies. In this article, the fixed-bed adsorption of pharmaceuticals on various adsorbents was reviewed. The experimental breakthrough curves of these pollutants under various flow rates, inlet concentrations, and bed heights were examined. Fixed-bed data in terms of saturation uptakes, breakthrough time, and the length of the mass transfer zone were included. The three most popular breakthrough models, namely, Adams–Bohart, Thomas, and Yoon–Nelson, were also reviewed for the correlation of breakthrough curve data along with the evaluation of model parameters. Compared with the Adams–Bohart model, the Thomas and Yoon–Nelson more effectively predicted the breakthrough data for the studied pollutants.

1. Introduction

Pharmaceuticals as emerging pollutants have become a major concern because of their low biodegradability, high persistence, and facile bioaccumulation (Zhang et al., 2016a). These compounds include diverse groups, such as antibiotics, anti-inflammatory agents, blood-lipid regulators, and steroidal hormones (Sun et al., 2015; Peltzer et al., 2017). Hospitals, households, and drug factories are the main sources of pharmaceuticals in wastewaters (Nazari et al., 2016a). The continuous release of these pollutants into the environment significantly affects human health and aquatic systems (Lu et al., 2016). Thus, these pollutants must be eliminated from wastewater.

Several methods, including biodegradation (Zhou et al., 2017), electrocoagulation (Nariyan et al., 2017), ozonation (Gomes et al., 2017), ultrafiltration membrane (Sheng et al., 2016), and adsorption (Marques et al., 2017) have been used to treat pharmaceuticals. Among these methods, adsorption is the simplest, cheapest, and most versatile technique for holding these pollutants (Moro et al., 2017; Bhadra et al., 2016). Activated carbon (Calisto et al., 2017), biochar (Lin et al., 2017a), mesoporous silica (Liang et al., 2016), zeolite (Sun et al., 2017), chitosan (Kyzas et al., 2017), carbon nanotubes (CNTs) (Zhao et al., 2016), clays (Dordio et al., 2017), resin (Zheng et al., 2017), biomass wastes (Zhou et al., 2015), and graphene oxide (Shan et al., 2017) adsorbents have been effectively utilized to attract pharmaceutical pollutants from wastewaters.

Adsorption can be categorized by operation mode into batch and continuous adsorption (Dichiara et al., 2015). The former mode occurs in a closed system, whereas the second type occurs in an open operating system involving a fixed-bed column (Xu et al., 2013). The equilibrium and kinetic data obtained during batch adsorption represent inaccurate data for the proper design and optimization of fixed-bed columns (Kizito et al., 2016). Thus, continuous experiments are required to obtain practical information under flow conditions in terms of breakthrough curves (Zuo et al., 2016). The analysis of these data is useful for calculating the design parameters and identifying the best operating conditions in fixed bed column (Mondal et al., 2016).

Batch adsorption of pharmaceutical pollutants has been reviewed by several articles (Ahmed, 2017; Yu et al., 2016; Kubo and Otsuka, 2016; Wang and Wang, 2016; Akhtar et al., 2016; Kyzas et al., 2015; Ahmed et al., 2015). However, no review has been conducted on the fixed-bed adsorption of pharmaceuticals. Therefore, the present review focuses on the adsorption of pharmaceutical pollutants by continuous operation mode. Breakthrough curves of pollutants are reviewed under different fixed-bed conditions, including initial drug concentration, volumetric flow rate, and bed length. The experimental data of the breakthrough curves are also analyzed by various models, such as the Adams–Bohart, Thomas, and Yoon–Nelson models.

2. Pharmaceutical pollutants

Pharmaceuticals or drugs are extensively consumed to improve the health statuses of humans and animals (Cecconet et al., 2017; Klatte

* Corresponding author.
E-mail address: muthanna.ja@gmail.com (M.J. Ahmed).

https://doi.org/10.1016/j.ecoenv.2017.12.012
Received 14 October 2017; Received in revised form 6 December 2017; Accepted 8 December 2017

Table 1
Experimental breakthrough data for continuous adsorption of pharmaceuticals on various adsorbents under best flow conditions.

Adsorbent	Adsorbate	C_o (mg/L)	Q (mL/min)	H (cm)	t_b (min)	q_e (mg/g)	MTZ (cm)	Ref.
Commercial carbon	Atenolol	500	1.5	2	630	24.96	1.89	Sancho et al. (2012)
Olive stones carbon	Paracetamol	6.7	6	2.9	278	88.40	1.03	García- et al. (2015)
Raspberry carbon	Ibuprofen	10	1.5	3	1740	46.14	1.03	Dubey et al. (2014)
Raspberry carbon	Naproxen	10	1.5	3	1680	46.29	1.02	Dubey et al. (2014)
Raspberry carbon	Clofibric acid	10	1.5	3	1620	45.75	1.06	Dubey et al. (2014)
Carbon nanotube	Sulfamethoxazole	40	2	15	25.6	92.00		Tian et al. (2013)
Carbon nanotube	Sulfapyridine	40	2	15	25.5	123.4		Tian et al. (2013)
Commercial carbon	Flumequine	2.7	3	6	258	222.7	5.9	Sotelo et al. (2013)
Commercial carbon	Nalidixic acid	80	1	1	325	1595	0.72	Patiño et al. (2016)
Carbon nanotube	Nalidixic acid	80	1	1	150	583	0.67	Patiño et al. (2016)
Graphite	Nalidixic acid	80	1	1	10	62	0.93	Patiño et al. (2016)
Akaganeite-carbon	Doxycycline	27	1	1.1	108	13.40		Zhang et al. (2016a, b)
Coffee residue/Fe_3O_4	Tetracycline	100	10	2	85.9	181.0	1.05	Oladipo et al. (2016)
Bone char	Naproxen	10	3	15	78	0.113	1.94	Reynel- et al. (2015)
Walnut shell carbon	Cephalexin	100	4.5	2	117.1	211.8		Nazari et al. (2016b)
Commercial carbon	Diclofenac	10	3	4	252	184.7	3.64	Sotelo et al. (2012)
Wollastonite polymer	Salicylic acid	60	1	4.6	90	16.91		Meng et al. (2013)
Bamboo charcoal	Tetracycline	50	6.6	2	104	23.5	1.96	Liao et al. (2013)
Bamboo charcoal	Chloramphenicol	50	6.6	2	115	18.8	1.91	Liao et al. (2013)
Peach stones carbon	Ibuprofen	10	2	15	426	55	6.6	Álvarez- et al. (2016)
Peach stones carbon	Tetracycline	10	2	15	1446	132.6	6.0	Álvarez- et al. (2016)
Activated biochar	Ranitidine	200	2	3	63	12	1.424	Mondal et al. (2016)

et al., 2017). Common drugs are antibiotics, analgesics, anti-inflammatory agents, lipid regulators, hormones, and β-blockers (Taheran et al., 2016; Madikizela et al., 2017). These biologically active chemicals appear in effluents of hospitals, drug factories, and landfills (Ashfaq et al., 2017; Muter et al., 2017). Drugs have been categorized as hazardous pollutants because of their continuous release, stability, and negative effect on the environment (Choi et al., 2016; Mirzaei et al., 2017).

Antibiotics are commonly used pharmaceuticals that protect humans and animals against diseases and infection caused by bacteria (Yang et al., 2017). These chemicals have also been used to improve the growth of plants and animals (Yu et al., 2016). The most important antibiotics are tetracyclines (TCs), penicillins, sulfonamides, macrolides, and quinolones (Puckowski et al., 2016). The permanent presence of antibiotics in aquatic systems continually produces harmful bacteria (Acosta et al., 2016).

Analgesics and anti-inflammatory agents are drugs utilized to relieve pain and impede inflammation. The most known analgesics are acetaminophen and aspirin (Feng et al., 2013). Ibuprofen (IB), ketoprofen, diclofenac, and naproxen (NA) are common anti-inflammatory agents. Drugs belonging to the class of analgesics and anti-inflammatory agents are classified as hazardous contaminants because of their stability in aquatic systems (Tiwari et al., 2017).

Hormones are important drugs given their extensive use and hazardous effect on humans and animals. Common natural hormones include estrogens (Li, 2014), such as estriol along with its derivatives, whereas the synthetic counterpart is 17α-ethinylestradiol (Yang et al., 2017). Therefore, estrogens have been categorized as abundant pollutants. Their presence in wastewaters poses a significant hazard to ecosystems (Tiwari et al., 2017).

β-Blockers are extensively utilized drugs for treating cardiovascular diseases, such as angina and hypertension. These drugs include metoprolol (MTP), propranolol, and atenolol (Yang et al., 2017). MTP is a widely consumed drug (Dong et al., 2013), and its metabolism in the human body produces metoprolol acid and other derivatives that comprise about 85% of the urinary content. Metoprolol acid constitutes the main component of the MTP metabolite and can be produced from MTP by biodegradation (Evgenidou et al., 2015).

Lipid regulators represent important drugs that impede cardiovascular disease progression and reduce cholesterol concentrations to prevent heart diseases (Caracciolo et al., 2015). These drugs mainly consist of statins and fibrates. The first group of lipid regulators is rarely present in the environment because metabolites are the main source of statins (Gracia-Lor et al., 2012). By contrast, the second group decreases the amount of cholesterol by impeding lipoprotein formation. Clofibric acid and its derivatives are among the fibrates most frequently detected in waters (Patrolecco et al., 2013).

3. Fixed bed adsorption

Treatment techniques such as membrane filtration, chlorination, electro-oxidation, ozonation, and biodegradation have been applied in the removal of pharmaceuticals from wastewaters (Rivera-Utrilla et al., 2013). However, these methods present issues related to high operation and maintenance costs along with the formation of byproducts with greater toxicity than the original pollutants (Nielsen and Bandosz, 2016). On the other hand, adsorption method has the advantages of easy operation, low cost, high efficiency, and no risk of highly toxic byproducts (Yu et al., 2016). Compared to batch process, adsorption in fixed bed columns is a simple mode operation and effective treatment process (de Franco et al., 2017). Adsorption in fixed bed is capable to treat large volumes of drug solution and reach high removal efficiency. Moreover, it can be easily scaled up from a laboratory to an industrial application (Lemus et al., 2017).

In designing and optimizing adsorption processes, basic kinetic data in terms of breakthrough curves are required (Hussein and Ahmed, 2016). The breakthrough curve of an adsorbate in a continuous system is the plot of the outlet-to-inlet concentration (C/C_o) ratio against time (t) or throughput volume (Benstoem et al., 2017). This curve explains the dynamics of a continuous adsorption system. The behavior of the breakthrough curve is related to the shape of the adsorption isotherm and is affected by the diffusional stages within the fixed bed (Chu, 2010). A typical breakthrough curve includes the mass transfer zone (MTZ) where adsorption takes place. Breakthrough occurs at contact time t_b where $C/C_o = 0.05$ (Tan and Hameed, 2017). The experimental breakthrough data, including the saturation adsorption capacities, breakthrough times, and MTZ values, for the studied drugs under various fixed bed adsorption variables such as flow rates, initial concentrations, and bed lengths are summarized in Table 1. Considering these collected data, we deduce that the highest adsorption capacity, breakthrough time, and MTZ among the studied absorbents were achieved by activated carbon.