Science of the Total Environment 601–602 (2017) 857–864

Contents lists available at ScienceDirect

Science of the Total Environment

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

Comparative study on pharmaceuticals adsorption in reclaimed water desalination concentrate using biochar: Impact of salts and organic matter

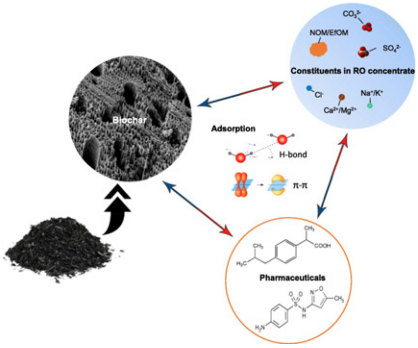
Lu Lin, Wenbin Jiang, Pei Xu *

Department of Civil Engineering, New Mexico State University, 3035 S Espina Street, Las Cruces, NM 88003, USA

HIGHLIGHTS

- Limited option of concentrate management is a barrier for water reuse & desalination.
- Biochar is a promising alternative adsorbent for organic contaminants removal.
- Biochar with larger surface area and pore volume has higher adsorption capacity.
- High ionic strength in concentrate increases ibuprofen & sulfamethoxazole removal.
- Carbonate species and organic matter hinder ibuprofen & sulfamethoxazole removal.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 29 March 2017
Received in revised form 21 May 2017
Accepted 22 May 2017
Available online 2 June 2017

Editor: D. Barcelo

Keywords:
Adsorption
Pharmaceuticals
Biochar
Activated carbon
Desalination concentrate
Water chemistry

ABSTRACT

The synergistic impact of salts and organic matter on adsorption of ibuprofen and sulfamethoxazole by three types of biochar and an activated carbon was investigated using reclaimed water reverse osmosis (RO) concentrate and synthetic solutions spiked with target organic compounds and non-target water constituents (e.g., Na^+, Ca^{2+}, Mg^{2+}, K^+, Cl^-, SO_4^{2-}, alkalinity, humic acid (HA), and bovine serum albumin (BSA)). Kinetic modeling was used to better understand the adsorption process between the carbon adsorbents and pharmaceuticals and to elucidate the impact of water chemistry on pharmaceuticals adsorption. The adsorption capacity of pharmaceuticals by biochar was affected by their physicochemical properties including ash content, specific surface area, charge, pore volume, as well as hydrophobicity, π-energy, and speciation of pharmaceuticals. The adsorption of pharmaceuticals in concentrate was pH-dependent, the kinetic rate constant increased with deceasing pH due to the electrical interactions between pharmaceutical molecules and adsorbents. High salinity and electrolyte ions in RO concentrate improved adsorption, whereas the presence of carbonate species, HA, and BSA hindered the removal of ibuprofen and sulfamethoxazole. This study revealed the correlation of concentrate water quality on adsorption of pharmaceuticals by biochar and activated carbon. Biochar provides a promising alternative to activated carbon for removal of organic contaminants of emerging concerns in various wastewater and concentrate streams.

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* Corresponding author.
E-mail address: pxu@nmsu.edu (P. Xu).

http://dx.doi.org/10.1016/j.scitotenv.2017.05.203
0048-9697/

1. Introduction

With the increasing freshwater demand and depleting conventional water resources, desalination of seawater, brackish water, and reclaimed water has been implemented to augment water supplies (Charcosset, 2009; IDA, 2016; Xu et al., 2010). Membrane technologies are the primary methods to remove dissolved solutes from impaired waters. During desalination, a concentrate stream is produced that contains high concentrations of dissolved salts and organic contaminants (Van der Bruggen et al., 2003; Xu et al., 2013). With the increasing use of desalination processes, concentrate management and disposal remains one of the major challenges associated with water reuse and desalination (Greenlee et al., 2009; Lin et al., 2016; Lin et al., 2017; Pérez-González et al., 2012; Miller, 2006). Treatment of desalination concentrate has the advantages of reducing concentrate volume for disposal, increasing water recovery, minimizing environmental impact, and reusing a waste stream (Lin et al., 2014; Xu et al., 2015).

Many organics concentrated in desalination concentrate are of considerable environmental concern (e.g., pharmaceuticals) and can hinder the beneficial use of concentrate. However, removal of these organics in concentrate is difficult because of its high salinity with total dissolved solids (TDS) concentration generally greater than 5000 mg/L and recalcitrant nature of the organic contaminants. The high ionic strength and some of the specific constituents can substantially affect process dynamics and reaction rates. For example, biological processes are typically adversely affected by high ionic strength (WHO, 2007). Conventional biological filters were only able to remove approximately 20% of total organic carbon (TOC) in reclaimed water desalination concentrate due to biopersistence of many organic compounds (Ng et al., 2008). Although carbon adsorption of effluent organic matter in RO concentrate could achieve over 90% removal (Dialynas et al., 2008; Zhou et al., 2011), granular activated carbon (GAC) is costly and mainly adsorbs organic fractions with small and medium molecular weight, and has lower affinity for large or hydrophilic organic compounds.

Recently, the application of biochar in soil amendment and water treatment has attracted significant attention (Chen et al., 2011; Inyang and Dickenson, 2015; Mohan et al., 2014; Spokas et al., 2012). Biochar is a porous carbon-residue derived from the thermal conversion of waste biomass under limited oxygen or anaerobic conditions. Most studies involve using biochar as a soil or landfill cover amendment where it can improve the productivity, carbon storage, and nutrient holding capacity (Inyang and Dickenson, 2015; Mohan et al., 2014; Spokas et al., 2012). Biochar can also be employed as an adsorbent due to its microporous structure, high carbon content, and specific surface area. In particular, the use of biochar for the removal of persistent organic pollutants from aqueous systems has been studied (Ahmad et al., 2012; Chen et al., 2008; Chen et al., 2015; Liu et al., 2012; Xie et al., 2014; Zheng et al., 2013). It has been reported some biochars have stronger adsorption and binding affinities to organic contaminants than commercial GACs (Ahmad et al., 2012; Tong et al., 2011). Moreover, biochar could be a low cost alternative because replacing or augmenting relatively more expensive, traditional adsorbents, such as GACs ($1500/ton), with biochar ($246/ton un-activated biochar) can reduce water treatment costs (Ahmad et al., 2012).

For example, Jung et al. studied adsorption of pharmaceuticals (sulfamethoxazole, carbamazepine, diclofenac, and ibuprofen) on chemically activated biochars from synthetic solution (Jung et al., 2013). The higher surface area and pore volume of oxygen-free activated biochar resulted in higher adsorption capacity towards endocrine disrupting compounds and pharmaceuticals (Jung et al., 2013). Batch isotherm experiments were conducted to study adsorption of the herbicide 2,4-dichlorophenoxyacetic acid to biochar from synthetic solution, and increasing pyrolysis temperature of biochar was found to positively influence adsorption capacity (Kearns et al., 2014). The potential use of biochar as a filter media for urban storm water runoff was evaluated and the results demonstrated that the biochar filter was effective to remove total suspended solids, nutrients, heavy metals, polycyclic aromatic hydrocarbons, and *E. coli.* (Mohanty and Boehm, 2014; Reddy et al., 2014). It was also reported that biochar has very high adsorption capacities of pharmaceutical (e.g., sulfamethoxazole) which may find use as an alternative sorbent for treating wastewater effluent (Yao et al., 2012). Tan et al. reviewed and summarized the various synthesis techniques for biochar-based nanocomposites and their effects on the decontamination of wastewater. Biochar-based nano-composites were able to remove organic contaminants including crystal violet, methylene blue, phenanthrene, phenol, sulfapyridine, naphthalene, and *p*-nitrotoluene from wastewater (Tan et al., 2016). Consequently, biochar is expected to have excellent potential as an adsorbent or filter media. Therefore, conventional unit operations and processes in potable and wastewater treatment for treating organic contaminants could utilize biochar to develop a cost-effective and environmental-friendly technology.

Up to date, most studies used synthetic solutions and storm water as water matrices for pharmaceuticals removal. There is lack of systematic study on the application of biochar for desalination concentrate treatment, as well as on the impact of water chemistry on biochar adsorption including salts and organic matter. Therefore, the overall objective of this research is to evaluate the adsorption capacity of biochar for the removal of pharmaceuticals from desalination concentrate. Two pharmaceuticals, ibuprofen and sulfamethoxazole, that are commonly used as anti-inflammatory drug and antibiotic for bacterial infections were selected as target contaminants. Adsorption of pharmaceuticals to various types of biochars in comparison with a commercial GAC was investigated using reverse osmosis (RO) concentrate collected from an advanced wastewater reclamation plant. Synthetic solutions spiked with model organic compounds (pharmaceuticals) and non-target water constituents (e.g., Na^+, Ca^{2+}, Mg^{2+}, K^+, Cl^-, SO_4^{2-}, alkalinity, humic acid (HA), and bovine serum albumin (BSA)) were also studied to simulate different types of wastewater and RO concentrate. The experiments and kinetic modeling allowed a better understanding of removal efficiency of the biochar, and elucidated the synergistic impact of salts and organic matter on biochar adsorption. The study aims to investigate the feasibility of biochar as a promising alternative to GAC for pharmaceuticals removal in various wastewater and concentrate streams.

2. Materials and methods

2.1. Materials and characterization

Three types of biochar were studied to compare their adsorption capacities for pharmaceuticals in RO concentrate. The biochar samples were obtained from Wakefield Agricultural Carbon LLC. (referred to as W-biochar), Cool Planet LLC. (referred to as C-biochar), and Green Texan Organic Farms LLC. (referred to as G-biochar), respectively. They were all produced through the thermal treatment of wood chips. A commercial GAC, NORIT® GAC 816 (effective size = 1.4 mm), was also studied for comparison. All adsorbent samples were washed four times with deionized water to remove impurities and water-soluble organic residuals. After drying at 105 °C for 24 h, they were sieved to a particle size distribution of 0.45–2 mm. Ash contents of the adsorbents were measured using ignition test by heating the adsorbents at 550 °C for 8 h (Furnace Vulcan 3-550, Dentsply International Inc., PA, USA). The zeta-potential was measured by SurPASS Electrokinetic Analyzer (Anton Paar GmbH, Graz, Austria). The BET (Brunauer, Emmett and Teller) specific surface area and pore volume of the adsorbents were measured using an extended pressure adsorption analyzer (ASAP 2050, Micromeritics Instrument Co., Norcross, GA).

The reclaimed water RO concentrate was collected from an advanced wastewater reclamation plant desalinating microfiltration permeate in City of Scottsdale, Arizona. The TDS concentration of the RO concentrate was 6.5 g/L with electrical conductivity of 10.1 mS/cm. The major ions in the RO concentrate included Na^+ (1920 mg/L),