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Effect of resin charged functional group, porosity, and chemical matrix on the long-term pharmaceutical removal mechanism by conventional ion exchange resins

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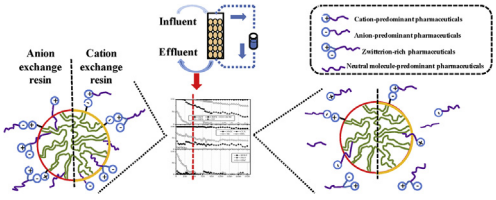
HIGHLIGHTS

- Twelve pharmaceuticals (10 classes, varied existing forms and hydrophobicities) were included.
- The long-term removal pharmaceutical mechanism by 5 resins during 8 cycles was clarified.
- Complex non-electrostatic interactions and electrostatic interactions simultaneously occurred.
- Non-electrostatic interactions resulted in differences in short- and long-term mechanisms.
- Resin porosity and chemical matrix had insignificant effect on long-term removal mechanism.

GRAPHICAL ABSTRACT



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ABSTRACT

This study attempted to clarify the long-term pharmaceutical removal mechanism from sewage treatment plant effluent during the cyclical adsorption-regeneration operation of 5 commercial resin-based fixed-bed reactors with the simultaneous occurrence of electrostatic interactions and complex non-electrostatic interactions. It examined 12 pharmaceuticals belonging to 10 therapeutic classes with different predominant existing forms and hydrophobicities. Furthermore, the effect of the resin charged functional group (strong-base vs. strong-acid vs. non-ionic), porosity (macroporous vs. gel), and chemical matrix (polystyrenic vs. polyacrylic) on the mechanism was investigated to optimize resin properties and achieve higher pharmaceutical removal. The results reported herein indicate the importance of non-electrostatic interactions between pharmaceuticals and the resin backbone during short-term cyclical operation (i.e., the 1st adsorption-regeneration cycle). With the development of cyclical operation, however, non-electrostatic interaction-induced pharmaceutical removal generally decreased and even disappeared when equilibrium was achieved between the influent and the resin. Despite pharmaceutical therapeutic class or hydrophilicity, anion (or cation) exchange resin preferentially removed those pharmaceuticals that were predominantly present as organic anions (or cations) by ion exchange process during long-term cyclical operation (i.e., $\geq$6 adsorption-regeneration cycles). Besides pharmaceuticals predominantly present as undissociated molecules, some amphoteric pharmaceuticals containing large amounts of zwitterions were also difficult to remove by ion exchange resin. Additionally, neither resin

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porosity nor chemical matrix had any significant effect on the long-term pharmaceutical removal mechanism.

1. Introduction

Based on their chemical structure, pharmaceuticals can be categorized into various classes such as antibiotics (e.g., β-lactam antibiotics, sulfonamides, fluoroquinolones and tetracyclines), psychiatric drugs, β-blockers, blood lipid regulators, anti-inflammatory analgesics, or endocrine disruptors. Introduction of pharmaceuticals into the environment via anthropogenic sources constitutes a potential risk for aquatic and terrestrial organisms, even at vestigial levels, in the foreseeable future. Potential problems include the dissemination of antibiotic resistance in human pathogens, the feminizing and masculinizing effects observed in animals, and etc. (Huber et al., 2005; Michael-Kordatou et al., 2015). Over the last two decades, pharmaceuticals have received growing international attention in public health as emerging micro-contaminants (Liu et al., 2014; Michael-Kordatou et al., 2015). Domestic consumption through prescription accounts for 60–80% of the total pharmaceutical consumption by humans, making urban wastewater the major input source of pharmaceuticals into the aquatic environment (Göbel et al., 2005; Huber et al., 2005). For the majority of pharmaceuticals, however, removal by conventional biological treatments is often inefficient in sewage treatment plants (STPs) (Castiglioni et al., 2006), which results in the significant presence of pharmaceuticals (e.g., ng L^{-1} to μg L^{-1} levels) in STP effluents worldwide (Zheng and Li, 2013; Bulloch et al., 2015). Therefore, the development of effective and economic tertiary treatment technologies to remove pharmaceuticals from STP effluents has become a research interest in recent decades (Xiao et al., 2014; Michael-Kordatou et al., 2015).

Most pharmaceuticals are weak organic acids or bases, which makes their sorption onto oppositely charged polymers even stronger than onto activated carbon (Bäuerlein et al., 2012). Many studies have highlighted the strong potential of commercial anion exchange resins (AERs) to remove pharmaceuticals from various water matrices (Michael-Kordatou et al., 2015) (e.g., MIEX® resins for seven sulfonamide antibiotics, seven tetracyclic antibiotics (Choi et al., 2007), estrone(Neale et al., 2010), triclosan, and sulfamethoxazole (SMX) (Huang et al., 2011); Lewatit MP500 resins for SMX and sulfamethazine (Fernández et al., 2014); Purolite A520E resins for diclofenac (DCF) (Landry and Boyer, 2013); Dowex 22 resins for DCF, ketoprofen, and naproxen (NPX), ibuprofen, paracetamol (Landry et al., 2015); IRA938, IRA958, IRA458, and IRA402 resins for nalidixic acid (Robberson et al., 2006); and Oasis MAX resin for caffeine and metformin (Bäuerlein et al., 2012)). Due to the presence of various functional groups (e.g., −OH, −COONa, $-SO_3Na$, −N═N−, and phenolic hydroxyl groups), many pharmaceutical molecules can simultaneously participate in both electrostatic interactions (i.e., Coulombic forces between the positively charged quaternary ammonium functional groups of AERs and the anionic moieties of pharmaceuticals) and various non-electrostatic interactions (Bäuerlein et al., 2012). These possible non-electrostatic interactions include van-der-Waals forces, H-bonding, hydrophobic, and π-π- interactions operating between the resin backbone and the non-ionic moieties of pharmaceuticals. For example, the high DCF removal by AER was attributed to the combination of Coulombic interactions, van der Waals interactions between the polystyrenic resin matrix and benzene rings of DCF, and possibly H-bonding between the dimethylethanol amine functional group side chain and the carboxylate and amine functional groups of DCF (Landry et al., 2015). Non-electrostatic interactions have often been demonstrated to significantly enhance pharmaceutical removal selectivity during AER treatment (Li and SenGupta, 2004; Landry and Boyer, 2013; Landry et al., 2015). In some cases, non-electrostatic interaction-dominated neutral resins are even more effective for pharmaceutical removal than AERs when these pharmaceuticals are undissociated (Robberson et al., 2006; Domínguez et al., 2011; Huang et al., 2012; Zhou et al., 2012).

The fixed-bed adsorption process is an ideal candidate for micropollutant removal due to the near-zero-level effluent, operational simplicity, and its adaptability to changing water flow rates and composition (Zheng et al., 2011), and has been used to remove pharmaceuticals from synthetic solution and ureolyzed human urine (Fernández et al., 2014; Landry et al., 2015). Based on a long-term pilot-scale operation (2.2 m^3 d^{-1}, 185 adsorption-regeneration cycles, 37,000 bed volumes, 1.5 years), we demonstrated the feasibility of using a commercial AER-based fixed-bed column to stably and effectively remove trace aromatic compounds (including pharmaceuticals) (as indicated by UV_{254} removal averaging 72%) and the whole genotoxicity from actual STP effluent at a low operational cost (Sun et al., 2015a, 2015b). It is interesting to find that obvious organic fouling on the AER had no significant influence on the long-term effective removals of dissolved organic matter (DOM), nitrogen, and phosphorus from STP effluent and resin physicochemical properties during the pilot-scale investigation (Sun et al., 2015a). This demonstrates that the AER-based fixed-bed column is one of the most promising strategies to selectively remove pharmaceuticals from STP effluent. During AER treatment, some pharmaceuticals behave more like organic anions, cations or zwitterions, whereas others behave more like undissociated molecules. Furthermore, due to the extreme complexity of non-electrostatic interactions, some pharmaceuticals coordinate weakly and are easy to elute from AERs, whereas others are strongly bound and would thus be difficult to elute (i.e., frequently observed organic fouling on AER (Sun et al., 2015a)). As demonstrated by UV_{254} removal averaging 72% observed in previous pilot-scale test (Sun et al., 2015a), the competition for sorption sites on AERs among various pharmaceuticals will significantly influence the removed pharmaceutical patterns during long-term adsorption-regeneration cyclical operation (i.e., the long-term pharmaceutical removal mechanism). In other words, some pharmaceuticals might be removed by the AER adsorption only during the short-term cyclic operation (i.e., the 1st adsorption-regeneration cycle), while other might remain being effectively removed even after a long-term cyclic operation (e.g., >6 adsorption-regeneration cycles). However, data from previous investigations are often limited to pharmaceutical adsorption equilibrium, kinetics, diffusion models, and breakthrough curves, and only consider anion-predominant pharmaceuticals, batch tests, or only 2-3 adsorption-regeneration cycles (Fernández et al., 2014; Landry et al., 2015), and is unable to explain the long-term pharmaceutical removal mechanism. At the same time, the heterogeneity of pharmaceuticals in STP effluent makes it very difficult to clarify long-term pharmaceutical removal mechanisms by the stoichiometry method, like those conducted in NOM removal