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Effect of inorganic regenerant properties on pharmaceutical adsorption and desorption performance on polymer anion exchange resin

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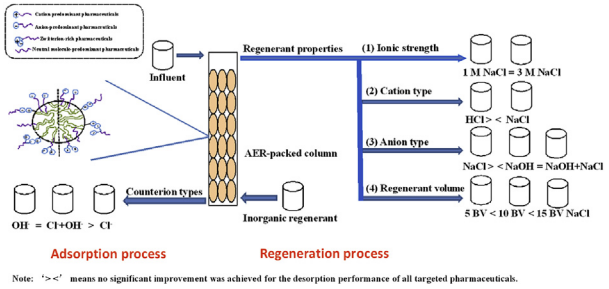
HIGHLIGHTS

- Mobile counterion types on AERs influenced pharmaceutical adsorption performance.
- Regenerant ionic strength insignificantly influenced pharmaceutical desorption performance.
- Regenerant cation or anion types influenced pharmaceutical desorption performance.
- Higher regenerant volume improved pharmaceutical desorption performance.

GRAPHICAL ABSTRACT



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ABSTRACT

This study investigated the potential effect of four frequently used inorganic regenerant properties (i.e., ionic strength, cation type, anion type, and regeneration solution volume) on the desorption and adsorption performance of 14 pharmaceuticals, belonging to 12 therapeutic classes with different predominant chemical forms and hydrophobicities, using polymeric anion exchange resin (AER)-packed fixed-bed column tests. After preconditioning with NaCl, NaOH, or saline-alkaline (SA) solutions, all resulting mobile counterion types of AERs effectively adsorbed all 14 pharmaceuticals, where the preferential magnitude of OH^--type = Cl^- + OH^--type > Cl^--type. During regeneration, ionic strength (1 M versus 3 M NaCl) had no significant influence on desorption performance for any of the 14 pharmaceuticals, while no regenerant cation (HCl versus NaCl) or anion type (NaCl versus NaOH and SA) achieved higher desorption efficiencies for all pharmaceuticals. A volumetric increase in 1 M or 3 M NaCl solutions significantly improved the desorption efficiencies of most pharmaceuticals, irrespective of ionic strength. The results indicate that regeneration protocols, including regenerant cation type, anion type and volume, should be optimized to improve pharmaceutical removal by AERs.

1. Introduction

Over the last two decades, the ubiquity of pharmaceuticals in the environment due to anthropogenic discharge has raised international concern over their potential risks to aquatic and terrestrial organisms (Huber et al., 2005; Michael-Kordatou et al., 2015).

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Domestic consumption of prescription medication accounts for 60–80% of the total pharmaceutical consumption by humans, making urban wastewater the major source of pharmaceuticals in the aquatic environment (Göbel et al., 2005; Huber et al., 2005). However, the majority of pharmaceuticals cannot be efficiently removed by conventional biological treatments in sewage treatment plants (STPs) (Castiglioni et al., 2006). More than ten therapeutic classes of pharmaceuticals (e.g., antibiotics, psychiatric drugs, β-blocker, blood lipid regulators, anti-inflammatory analgesics, and endocrine disruptors) are frequently detected at ng L^{-1} and even μg L^{-1} levels in STP effluent, worldwide (Zheng and Li, 2013; Bulloch et al., 2015). Therefore, recent research has focused on developing effective and economic pharmaceutical discharge control technologies for STP effluent (generally at neutral pH levels) (Xiao et al., 2014; Michael-Kordatou et al., 2015).

When adsorbing onto polymer anion exchange resin (AER), many pharmaceutical molecules simultaneously participate in electrostatic interactions (i.e., Coulombic forces between positively charged quaternary ammonium functional groups of AERs and anionic moieties of pharmaceuticals) and non-electrostatic interactions (e.g., van der Waals forces, H-bonding, hydrophobicity, and π-interactions between the resin backbone and non-ionic moieties of pharmaceuticals) with their functional groups (e.g., −OH, −COONa, $-SO_3Na$, −N═N−, and phenolic hydroxyl groups) (Bäuerlein et al., 2012; Landry et al., 2015). AER treatment is expected to be an effective process for selectively removing pharmaceuticals from various water matrices, as they have much better adsorption and regeneration performance than activated carbon (Bäuerlein et al., 2012; Landry and Boyer, 2013). Many recent studies have highlighted the high potential of commercial AERs to adsorb pharmaceuticals, including sulfonamide antibiotics (Choi et al., 2007; Huang et al., 2011; Fernández et al., 2014), tetracyclic antibiotics (Choi et al., 2007), estrone (Neale et al., 2010), triclosan (Huang et al., 2011), diclofenac (DCF) (Landry and Boyer, 2013; Landry et al., 2015); ketoprofen, naproxen (NPX), ibuprofen, acetaminophen (ACM) (Landry et al., 2015), nalidixic acid (Robberson et al., 2006), caffeine, and metformin (Bäuerlein et al., 2012). Using a long-term pilot-scale operation (2.2 m^3 d^{-1}, 185 adsorption-regeneration cycles, 37,000 bed volumes (BV), 1.5 years), we demonstrated the feasibility of using a commercial AER-packed fixed-bed column to stably and effectively remove trace aromatic compounds, including pharmaceuticals (as indicated by UV_{254} and SUVA removals averaging 72 and 55%, respectively), and the overall genotoxicity of actual STP effluent at a low operational cost (Sun et al., 2015a, 2015b). Over the 185 adsorption-regeneration cycle operation, organic substances, nitrogen, and phosphorus adsorbed onto the AERs were effectively eluted and stably enriched into the NaCl solution (Sun et al., 2015a). Subsequently, we further investigated the potential 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 long-term pharmaceutical removal mechanism (Wang et al., 2016). These results demonstrated that the AER-based fixed-bed adsorption process is one of the most promising strategies for selectively removing pharmaceuticals from STP effluent.

According to manufacturer recommendations, exhausted AERs are often regenerated through counterion exchange with inorganic regenerants (e.g., NaOH, HCl, or NaCl solutions) in most cases, where any anions sorbed onto quaternary ammonium functional groups are substituted for Cl^- or OH^- ions (Kitis et al., 2007; Bassandeh et al., 2013). Research has examined various NaCl concentrations (4–12% (m/m)) (Landry and Boyer, 2013; Shuang et al., 2013) and NaCl/NaOH mixtures (i.e., saline-alkaline (SA) solutions) (Neale et al., 2010; Shuang et al., 2013). Our previous investigation also demonstrated that NaCl solution could effectively elute pharmaceuticals adsorbed on AERs during the long-term adsorption-regeneration cycles of the AER-packed fixed-bed column test for STP effluent (Sun et al., 2015a; Wang et al., 2016). Under these conditions, incomplete organic regeneration efficiencies are frequently observed due to irreversible organic adsorption, for example, 74–93% for biological treated paper mill effluent (Bassandeh et al., 2013), 40–70% for estrone (Neale et al., 2010), and 24% for DCF (Landry and Boyer, 2013). It is well known that optimizing AER regeneration protocols can improve AER adsorption capacity, effectively reducing the fresh resin dosage, regeneration frequency, and waste regeneration effluent volume (Shuang et al., 2013). However, it is not known if the regeneration process for pharmaceutical desorption with inorganic regenerants only reverses organic compounds adsorbed by ion exchange or also by other processes. The potential effects of regenerant water chemistry (e.g., ionic strength, cation type, and anion type) and regeneration solution volume on desorption performance of pharmaceuticals with various therapeutic classes and predominant chemical forms must be determined. Furthermore, comprehensive evaluations are limited with respect to the potential effects of the different mobile counterion types formed with different inorganic regenerants, including Cl^--, OH^--, and $Cl^- + OH^-$-types, on pharmaceutical adsorption performance. These shortcomings restrict AER regeneration optimization of the AER-packed fixed-bed adsorption process, which could further improve pharmaceutical removal from STP effluent.

Our previous investigations demonstrated that neither AER porosity nor chemical matrix had any significant effect on the long-term pharmaceutical removal mechanism when, which was helpful to optimize resin properties to achieve higher pharmaceutical removal from STP effluent (Wang et al., 2016). Based on these results, using 14 pharmaceuticals belonging to 12 therapeutic classes with different chemical forms and hydrophobicities, we systematically investigated the potential effect of inorganic regenerant properties (i.e., ionic strength, cation type, anion type, and regeneration solution volume) on the pharmaceutical desorption and adsorption performance using AER-packed fixed-bed column tests in this study. An automated solid phase extraction-high performance liquid chromatography-electrospray ionization tandem mass spectrometry (ASPE-HPLC-ESI-MS/MS) method was developed to quantify pharmaceutical concentrations in different water matrices sampled during adsorption and desorption tests. Because pharmaceuticals within therapeutic classes often have similar chemical structures, physicochemical properties (e.g., $\log K_{ow}$ and pK_a), and adsorption performances in AERs (Choi et al., 2007), only one or two pharmaceuticals were selected to represent therapeutic classes in this study.

2. Materials and methods

2.1. Pharmaceutical standards, synthetic solutions, and commercial AER

The molecular structure, CAS registration number, molecular weight, water solubility, pK_a, and $\text{Log}K_{ow}$ of the 14 pharmaceuticals used in this study are listed in Table S1. Sulfamethoxazole (SMX), ACM, NPX, bezafibrate (BZF), 17β-estradiol (E2), and bisphenol A (BPA) standards were purchased from Tokyo Chemical Industry (Shanghai, China). Cephalexin (CLX), erythromycin (ERY), trimethoprim (TMP), ofloxacin (OFL), and propranolol (PRO) standards were purchased from Toronto Research Chemicals (Toronto, Canada). Tetracycline (TC), carbamazepine (CBZ), and sulpiride (SULP) were purchased from Johnson Matthey (Cambridge, UK), Acros Organics (Morris Plains, NJ, USA), and Sigma Aldrich (St. Louis, MO, USA), respectively. The purities of all analytical standards used in