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Palygorskite for the uptake and removal of pharmaceuticals for wastewater treatment

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ABSTRACT

In this study, ranitidine (RT), a cationic drug was tested for its removal by palygorskite (PA) under different physico-chemical conditions, such as initial RT concentrations, contact time, equilibrium solution pH, ionic strength, and temperature. FTIR, SEM, and XRD analyses were conducted to determine the mechanisms of RT uptake on PA. The results showed that cation exchange or electrostatic interactions between the negatively charged PA surfaces and positively charge dimethylamine of RT was the major mechanism of RT uptake when solution pH was less than the pK_a value of RT. Under high pH conditions, the 2,5-disubstituted furan group interacted with the PA surface via a delocalized π -bond, suggesting that the RT molecules were parallel to PA surface. The larger values for the RT distribution coefficient between PA and solution via electrostatic or cation exchange interactions and delocalized π -bonds in a multi-regression analysis confirmed these mechanisms. The XRD results showed no expansion of the (110) reflection of PA while the SEM observation showed no changes in crystal size and morphology, indicating that the sites for RT uptake were limited to the external surfaces of PA.

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1. Introduction

Sorptive removal is an important approach in wastewater treatment. As zeolites have larger specific surface area (SSA) and high cation exchange capacity (CEC), they were studied extensively for their sorptive removal of ammonium, heavy metals, and other organic contaminants (Wang and Peng, 2010). Similarly, many clay minerals also have large SSA and high CEC. Among the clay minerals, bentonites have been studied the most in wastewater treatment for the removal of heavy metals (Viraraghavan and Kapoor, 1994) as well as dyes (Hu et al., 2006), due to their large surface, inter-layer accessibility, and extreme effectiveness in contaminant removal.

Because of extensive use and misuse of pharmaceuticals and personal care products (PPCPs) in human health and animal husbandry, wastewater usually contains pharmaceuticals either as excretion products resulting from metabolism or as a consequence of inaccurate disposal of unused or out-of-date drugs (Carucci et al., 2006). Due to recent advancements in analytical technology, more and more PPCPs were detected in surface water and even in the effluents of wastewater treatment plants (WWTPs). Commonly found pharmaceuticals include antibiotics, β -blockers, and hormones. They could be in cationic, zwitterionic, or anionic forms, or in hydrophobic organic molecules.

For the removal of cationic pharmaceuticals, adsorbents with large SSA and high CEC are advantageous. Palygorskite

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(PA) is a special type of clay made of periodic reversal of the building block so that the interlayer space is made of one-dimensional channel, thus limiting its expandability. As an adsorbent, most studies on PA were conducted for the removal of heavy metals and dye stuff (Galan, 1996; Sanchez et al., 1999; Taha and Mohammed, 2013). In addition, PA was also tested for the removal of organic compounds. The most important example of using palygorskite as an adsorbent is Maya Blue. Sorption of indigo in the palygorskite channel resulted in the longevity of the blue dye (Chiari et al., 2003). Meanwhile, PA was also studied as additives for drug formulations and was used in antacid, gastrointestinal protector, antidiarrhoeic, cosmetic creams, powders, and emulsions (Carretero and Pozo, 2010). In addition, it was used as drug excipient as disintegrant, diluent and binder, emulsifying, thickening and anticaking agent, flavor corrector, and carrier-releaser of active principles (Carretero and Pozo, 2009). More recently it was studied for the sorptive removal of tetracycline (TC) from water (Chang et al., 2009). In addition to using PA in its raw form, PA could be combined with polypyrrole to form nanocomposite for the collection of Cr(VI) (Yao et al., 2012) and for tunable drug delivery (Kong et al., 2014), or to be incorporated with poly(m-phenylenediamine) to form nanocomposite materials for the enhanced removal of Cr(VI) (Xie et al., 2014). However, before PA could be applied in more general way for wastewater treatment, particularly for the removal of PPCPs, more studies on its efficiency and removal mechanisms are needed.

Ranitidine (RT) is a selective H₂-receptor antagonist and powerful inhibitor of gastric acid secretion introduced for the treatment of peptic ulcers and related disorders (Dumanović et al., 1997). It is a drug responsible for disturbing the microbial ecology of surface waters (Savci, 2013). RT was 100% detected in 110 biosolids samples collected by the U.S. Environmental Protection Agency (EPA) in its 2001 National Sewage Sludge Survey (McClellan and Halden, 2010). Its concentrations in biosolids were in the range of 1–10 mg/kg (Deo and Halden, 2013).

Inconsistent overall removal of RT was reported in different WWTPs with the efficiency as high as 80% and as low as only 30% (Jelic et al., 2011). In an experiment to study the biological treatability of pharmaceuticals and their potential toxic effect in biological processes, RT showed generally low removal efficiencies (17–26%) and its adsorption on activated and inactivated sludge was only 15 and 0% (Carucci et al., 2006). A distribution coefficient (K_d) value of 0.42 L/g was found for RT sorption on bacteria cells, however, the contribution of sorption and biodegradation to the overall RT removal was 4.76 and 0.15% (Vasiliadou et al., 2013). Moreover, in the presence of UV-C radiation the RT removal rate was increased with the addition of H₂O₂ promoters while the use of photocatalyst TiO₂ negatively affects the process (Rivas et al., 2010).

RT was markedly adsorbed by smectite and was independent of pH (Vatier et al., 1994). Phosphated cellulose was also considered as an efficient biomaterial for RT removal from aqueous solution (Bezerra et al., 2014). However, there has been no report on using PA for the removal of RT. The goal of this study was to test the overall removal efficiency of cationic drugs using RT as a representative drug and PA as an adsorbent under different physicochemical conditions and to decipher the mechanisms behind the RT removal by PA. As this is part of larger study on interactions between Earth materials and anthropogenic contaminants, it is anticipated that the results would add practical values to the use of Earth materials,

particularly clay minerals in wastewater treatment of emerging compounds.

2. Materials and methods

The palygorskite (PA) was purchased from the Clay Mineral Repository in Purdue University. It has a CEC value of 175 mmol_c/kg (Borden and Giese, 2001) and an SSA of 173 m²/g (Dogan et al., 2006). It has about 80% PA, 10% smectite, 7% quartz, 2% feldspar, and 1% others (Chiperă and Bish, 2001). It is a good sorbent for a variety of compounds due to its large SSA and moderate CEC values. Although it has significant amount of other minerals, it is listed as a standard clay mineral. For the sake of parameter comparison, it was used without pre-treatment.

The representative pharmaceutical compound was ranitidine (RT) or N-[2-[[[5-1((dimethylamino)methyl]-2-furanyl)methyl]thio]ethyl]-N'-methyl-2-nitro-1,1-ethenediamine (Hohnjec et al., 1986), in the HCl form (CAS# 66357-59-3). It can exist as form I or form II (Wu et al., 2000). It has a molecular weight of 350.86 g/mol. It has an octanol-water partitioning coefficient close to 2 (logP ~ 0.3; Moffat et al., 2004). It is freely soluble in water and stable in aqueous solutions. In 0.9% NaCl solution above 95% RT remain for up to 28 days (Galante et al., 1990). However, it is unstable in low pH buffer solutions with less than 20% remained after 40 h storage at 65 °C (Teraoka et al., 1993).

A pK_a value of 8.2 was reported (Cholerton et al., 1984; Balasubramaniam et al., 2008). However, two pK_a values at 2.3 and 8.2 (Castela-Papin et al., 1999; Djabri et al., 2012) or 1.95 and 8.13, corresponding to the protonation of 2-nitroethene diamine and dimethyl amino group (Dumanović et al., 1997) were also reported. Thus, it exists primarily as a monovalent cation between pH 4 and 7 (Djabri et al., 2012), where the dimethyl amino group was protonated (Dumanović et al., 1997). When solution pH was below the pK_{a1}, the 2-nitroethene diamine group is also protonated (Dumanović et al., 1997).

In all experiments, 0.2 g of PA was combined with 10 mL of RT aqueous solution in 50 mL centrifuge tubes. For the isotherm study, the initial RT concentrations varied from 0 to 4 mM. For all other tests, 1.2 mM was used. The mixtures were shaken at 150 rpm for 24 h, with the exception of the kinetic study, and then centrifuged at 3500 rpm for 10 min, and the supernatants were passed through 0.45 μm PTFE syringe filters before being analyzed for the equilibrium RT concentrations using an UV-vis method. The amount of RT adsorbed was calculated by (C_{final} - C_{initial}) × volume of liquid/mass of solid. The equilibrium solution pH was 7.3–7.8 for the supernatant, but not adjusted except for the pH study. In the kinetic experiment, the samples were shaken for 0.25, 0.5, 1.0, 2.0, 4.0, 8.0, and 24 for the kinetic study. For the pH study, the equilibrium solution pH was adjusted to values between 4 to 10, using minute amounts of 1 M HCl or NaOH. For ionic strength tests, the solution was adjusted to reach NaCl concentrations of 0.001, 0.01, 0.1, and 1.0 M. The temperature study was conducted in a Hybaid Micro-4 hybridization oven rotator incubator and the temperature was maintained at 32, 42, and 52 °C.

The equilibrium solution concentrations of RT were measured by UV-vis at a wavelength of 312 nm as its peak absorbance values were reported at 226 and 312 nm (Hohnjec et al., 1986; Sokol et al., 2011), 229 and 315 nm (Dash et al.,

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