Palygorskite for the uptake and removal of pharmaceuticals for wastewater treatment

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**A R T I C L E   I N F O**

Article history:
Received 15 March 2015
Received in revised form 31 August 2015
Accepted 11 September 2015
Available online 25 September 2015

**Keywords:**
Cation exchange
Pharmaceutical removal
Palygorskite
Ranitidine
Sorption
Wastewater

**A B S T R A C T**

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\textsubscript{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 (1 1 0) 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, interlayer 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...
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 staff (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, anti-diarrhoeic, 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-release 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 polypropylene 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 (Kd) 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% (Vasilidou 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 mmolc/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 (Chiperia 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-[[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 ~ 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 40h storage at 65 °C (Teraoka et al., 1993).

A pKa value of 8.2 was reported (Cholerton et al., 1984; Balasubramaniam et al., 2008). However, two pKαι values at 2.3 and 8.2 (Castella-Papin et al., 1999; Djabri et al., 2012) or 1.85 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 7 and 4 (Djabri et al., 2012), where the dimethyl amino group was protonated (Dumanović et al., 1997). When solution pH was below the pKαι, 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∞ − Cinitial) x 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 Hybrid 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.,
A wavelength of 227 nm (Grimming and Pluta, 2000) or 229 nm was also used (Savci, 2013). The isosbestic point for RT was 243 nm in strong acid solution and 240 and 292 nm in strong alkaline solution, but the absorbance at 313 nm was stable over pH 3.5–12 range (Dumanović et al., 1997).

The FTIR spectra were acquired from 600 to 4000 cm⁻¹ by accumulating 256 scans at a resolution 4 cm⁻¹ using a Jasco FT/IR-4100 Spectrometer equipped with a ZnSe crystal and Attenuated Total Reflection accessory.

The powder X-Ray diffraction (XRD) analyses were carried out using a D8 ADVANCE diffractometer (Bruker Corp.) under a CuKα radiation at 40 kV and 40 mA. Samples were scanned from 2 to 40° 2θ with a scanning speed of 0.01°/s. The scanning electron microscope (SEM) imaging was performed on an FEI Quanta 250 FEG SEM operated at an accelerating voltage of 7 kV. The specimens were Pt-coated for SEM observations but carbon-coated for X-ray energy-dispersive spectroscopy (EDS) analyses. For the EDS work, an accelerating voltage of 15 kV for the electron beam was used.

3. Results and discussion

3.1. RT removal as affected by initial RT concentrations

The RT removal increased as the initial RT concentrations increased. When the amounts of RT removal were plotted against the equilibrium RT concentrations, the Langmuir model described the data better (Fig. 1). It has the formula:

$$C_S = \frac{K_L S_m C_i}{1 + K_L C_i}$$  \hspace{1cm} (1)

where $C_S$ is the amount of RT removed at equilibrium (mmol/kg), $S_m$ the apparent removal capacity (mmol/kg), $C_i$ the equilibrium RT concentration (mmol/L), and $K_L$ the Langmuir coefficient ($L$/mmol), reflecting the affinity of the solute for the substrate. Eq. (1) can be re-arranged into a linear form

$$\frac{C_i}{C_S} = \frac{1}{K_L S_m} + \frac{C_i}{S_m}$$  \hspace{1cm} (2)

so that $K_L$ and $S_m$ can be determined by a linear regression. The fitted RT removal capacity was 156 mmol/kg, slightly less than its CEC value of 175 mmol/kg (Borden and Giese, 2001). The uptake of TC by the same PA was 206 mmol/kg (Chang et al., 2009). In comparison, an RT removal capacity of 610 mmol/kg by diosmetite was reported previously and the RT removal capacity increased with increasing solution pH (Castella-Papin et al., 1999).

Compared to PA in this study, RT removal by sucralfat followed a Freundlich isotherm with the $K_f$ and $n$ values of 6.7 and 0.99; 24 and 1.5; and 18 and 1.0 at pH 1.5, 3.6, and 5.0 (Griming and Pluta, 2000). RT sorption on live activated sludge resulted in $K_f$ and $n$ values of 0.1 mg/g/L/mg¹/₉ and 0.9 (Savci, 2013). A recently study of RT adsorption on Lagenaria vulgaris based carbon resulted in a capacity of 315 mg/g (Bojić et al., 2015). The calculated log $K_{ow}$ for RT varied from 1.8 to 3.0 (Savci, 2013).

3.2. Kinetics of MT removal

RT sorption on PA was instantaneous even at the shortest contact time of 0.25 h (Fig. 2). This quick sorption may indicate external sorption sites for RT removal from water. The instantaneous RT removal suggests that the best practice for the removal of ionic pharmaceuticals can be achieved using clays with high CEC values. Similarly, instantaneous uptake of TC was found on the same PA (Chang et al., 2009).

3.3. Influence of solution pH on RT removal

Solution pH had strong influence on RT removal by PA (Fig. 3). When equilibrium solution pH was below 8.2, the RT removal increased slightly with increasing pH. This slight increase could be attributed to the slight increase in negative charges of PA due to deprotonation as pH increased. On the contrary, a drastic decrease in RT removal was observed as solution pH increased from 8.2 to 10. The coincidence of the $pK_a$ value

![Fig. 1 – Uptake of RT on PA. The solid line is the Langmuir fit to the observed data.](image1)

![Fig. 2 – Kinetics of RT uptake on PA.](image2)

![Fig. 3 – Uptake of RT on PA as affected by equilibrium solution pH. The inset is the multivariable regression fit of $K_d$ components to the experimental data.](image3)
of RT and the decrease in RT removal suggested that electrostatic interaction or cation exchange might be the dominant mechanism for RT removal by PA. Previous results showed that RT intercalation in the interlayer of montmorillonite (MMT) was pH dependent and peak intercalation was found at pH 4–8 (Joshi et al., 2010). RT was markedly adsorbed by smectite, independently of solution pH (Vatier et al., 1994).

The contribution of each interaction to the overall $K_d$ value could be linked to the mass fraction ($\omega$) of each species of RT by:

$$K_d = K_d^{PA+RT} + K_d^{PA–RT} + K_d^{PA} + K_d^{RT}$$

where the superscripts $PA+RT$, $PA–RT$, and $PA$ represent interactions between positive charges on edges of PA due to broken bond effect and positively charged RT, negatively charged PA surfaces and positively charged RT, and negatively charged PA and neutral RT, respectively. The fitted results by a multivariable regression were $-32, 304,$ and $-208$ L/kg, for $K_d^{PA+RT}$, $K_d^{PA–RT}$, and $K_d^{PA}$, respectively, with an intercept of 250 L/kg (Fig. 3). The extremely larger value of $K_d^{PA+RT}$ and extreme negative value of $K_d^{PA–RT}$ again confirmed the electrostatic or cation exchange interactions. The substantial intercept value may be attributed to interactions other than electrostatic or cation exchange.

### 3.4. Influence of solution ionic strength

As the NaCl concentration increased from 0.001 to 1 M, the RT removal decreased from 53 to 43 mmol/kg (Fig. 4). The free energy of sorption $\Delta G$ could be calculated from $K_d$ by:

$$\Delta G = -RT \ln K_d$$

where $R$ is the gas constant and $T$ is the reaction temperature in K. The $\Delta G$ values increased from $-15$ to $-12$ for RT removal by PA as the NaCl concentration increased from 0.001 to 1 M, respectively. Similarly, $\Delta G$ values increased from $-16$ to $-14$ for TC removal by the same PA as the NaCl concentration increased from 0.001 to 1 M, respectively (Chang et al., 2009).

In comparison, the $\Delta G$ was 3.6 to 4.5 kJ/mol for RT sorption on activated biosludge (Savci, 2013) and was $-3$ to $-13$ kJ/mol for RT sorption on L. vulgaris based carbon depending on the initial RT concentrations (Bojić et al., 2015). The moderate negative $\Delta G$ values suggested physi-sorption such as cation exchange or electrostatic interactions. On a separate study, expired RT showed inhibitive effect for mild steel in acid medium and its sorption on the mild steel surface resulted in $\Delta G$ values of $-37$ to $-40$ kJ/mol and $\Delta H$ values of $-10$ kJ/mol at 303–333 K, suggesting chemisorption on mild steel (Hameed, 2011).

### 3.5. Influence of temperature

Overall, the influence of temperature on RT removal by PA was minute. The $\Delta G$ values were in a narrow range of $-14.8$ to $-13.3$ kJ/mol for RT removal as the temperature increased from 32 to 52 °C (Fig. 5). Also, the RT removal by PA was exothermic with $\Delta H$ values at $-36$ and $-18$ kJ/mol and $\Delta S$ values were $-0.04$ and $0.01$ kJ/mol*K when the initial RT concentrations were 0.6 and 1.2 mM, respectively. In comparison, the uptake of TC on the same PA was endothermic (Chang et al., 2009). The $\Delta G$ values for RT adsorption on superheated steam activated carbon derived from mung bean husk was in the range of $-30$ kJ/mol ( Mondal et al., 2015).

### 3.6. FTIR analysis

There are two polymorphs for RTHCl (Wu et al., 2000). The melting points for these two forms were 144.5 and 146.2 °C (Cholerton et al., 1984). While no conversion from form I to form II was noticed over storage, but pretreatment of form I with water following drying resulted in the formation of a mixture of form I and form II (Wu et al., 2000).

The FTIR spectrum of crystalline RT (Fig. 6a) matched well with that of form II reported earlier (Cholerton et al., 1984; Hohnjec et al., 1986). The 2971 and 2918 cm$^{-1}$ were attributed to the C–H aliphatic bond. The bands in the 2700–2300 and 1620–1570 cm$^{-1}$ region were assigned to NH absorption of the protonated dimethylamino group (Cholerton et al., 1984). In the IR spectra of MMT–RT hybrid, the bands at 2400 cm$^{-1}$ (C=NH) and 1610 cm$^{-1}$ (C–N) were shifted to 2357 and 1627 cm$^{-1}$, respectively, signifying the strong interaction of RT with the MMT layers (Joshi et al., 2010). In contrast, the IR spectrum of physical mixture of aceclofenac and RTHCl showed no shift of any of these characteristic bands, indicating no chemical interaction between them (El-Nabarawi et al., 2013). In this study, they were located at 2449 and 1616 cm$^{-1}$ for crystalline RT, respectively. The band at 2449 cm$^{-1}$ was not resolved after RT uptake on PA, while the 1616 cm$^{-1}$ band was shown as broader bands at 1637, most likely due to contribution

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Fig. 4 – Uptake of RT on PA (open symbols with the left axis) and free energy of adsorption (closed symbols with the right axis) as affected by solution ionic strength.

Fig. 5 – Uptake of RT as expressed by Ln($K_d$) (left axis and blue) and the change in free energy of adsorption (right axis and red) from initial RT concentrations of 0.6 and 1.2 mmol/L as affected by temperature (For interpretation of the references to colour in this figure legend and the text, the reader is referred to the web version of this article.).
of OH from water at 1650 cm\(^{-1}\), suggesting that the dimethylamine group was no long protonated.

As RT is a secondary amine, it may protonate into a tertiary amine group R\(_3\)-NN\(^+\) showing a band at 2560 cm\(^{-1}\) after in contact with Eudragit E100, which suggested a mild interaction, such as hydrogen bonding, between the protonated tertiary amine group and the polymer (Bharate et al., 2010). In this study, this band was located at 2546 cm\(^{-1}\), suggesting it was a tertiary amine group R\(_3\)-NN\(^+\) when RT was in crystalline form II and it disappeared after RT uptake onto PA, again indicating that the positive charge was compensated by the negatively charged PA surfaces after RT uptake.

The band at 1376 cm\(^{-1}\) was assigned to NO\(_2\) group, and the one at 1240 cm\(^{-1}\) to C–N bond (Jamróżyewicz and Lukasjak, 2009). These bands were characteristics of a nitro group attached to a substituted ethene group and would not be visible in form I (Hohnjec et al., 1986). In this study, they were shown as broader band at 1380–1440 cm\(^{-1}\), suggesting that the participation of N–H bond or NO\(_2\) group for the uptake of RT on PA (Fig. 6b).

The bands at 1015 and 790 cm\(^{-1}\) were attributed to a 2,5-disubstituted furan (Cholerton et al., 1984). In this study, they were located at 1045 and 798 cm\(^{-1}\) and shifted to 1081 cm\(^{-1}\) and 873 cm\(^{-1}\) with increasing intensities as the amount of RT uptake on PA increased (Fig. 6b). With the same input RT concentration, equilibrium solution pH did not have any influence on the intensities of these two bands (data not shown). This explains the large intercept value for the \(K_d\) fitting using Eq. (3) and suggests significant contribution by the 2,5-disubstituted furan group for RT uptake on PA.

From above, it can be concluded that part of the interactions between PA and RT was from the 2,5-disubstituted furan via a delocalized \(\pi\)-bond, suggesting that the RT molecules were parallel to PA surface. As the delocalized \(\pi\)-bond is not affected by solution pH, this delocalized \(\pi\)-bond interaction between the RT molecules and the PA surfaces might be responsible for the large intercept values of \(K_d\) determined from the multi-regression analyses in pH studies or for the RT uptake at solution pH greater than the \(pK_a\) value. With the RT in form II, the OH attached to N might form hydrogen bond with the O on the surface of PA for part of the uptake of RT, which may also contribute to the large intercept from the non-linear regression using Eq. (3).

The protonation of 2-nitroethene diamine and dimethyl amino group (Dumanović et al., 1997) may result in formation of RT cations that could cation exchange with inorganic cations on PA surfaces. This cation exchange process should be responsible for the large \(K_{PA-RT}^{-1}\) value. Uptake of TC on the same PA was attributed to cation exchange as confirmed by the quantitative desorption of exchangeable cations accompanying TC uptake (Chang et al., 2009).

One characteristic feature revealed by the FTIR data is the increase of absorbance value of the 3350 and 1650 cm\(^{-1}\), suggesting an increase in water contents after RT uptake on PA. Precious results also showed that RT mixed with purified talc and magnesium stearate could absorb up to 5% moisture after in contact with an air of 75% relative humidity for 150 min (Islam et al., 2008).

Energy minimization revealed that RT was a flat molecule with a dimension of 1.73 nm long by 0.55 nm wide, resulting in a surface area of 1.0 nm\(^2\). When the SSA of 173 m\(^2\)/g was used, at the RT uptake capacity of 156 mmol/kg, the available surface area was 1.6 mm\(^2\) per RT molecule. Considering that the RT uptake capacity was close to the CEC value of PA, the limiting factor for RT uptake on PA might be the CEC value instead of SSA. The SEM observations of PA showed no changes in crystal morphology, nor in crystal size before and after in contact with 4 mM RT (Fig. 7). This may indicate no changes in SSA and confirms that the uptake of RT is on the external sites of PA.
The EDS measurement of relative element contents revealed no obvious changes in metal cations except an increase in C content after RT uptake (Fig. 7). The results from XRD analyses confirmed that that RT was in form II on one hand and showed no change in the d-spacing of the (110) reflection of PA, further confirming surface adsorption instead of intercalation on the other hand (Fig. 8). Similarly, the uptake and retention of TC was also limited to the CEC rather than the external surfaces of PA and was on the external surfaces of PA as well (Chang et al., 2009).

The significant uptake of RT by PA suggests that PA could be a good additive, in addition to bentonite, for wastewater treatment for the removal of cationic drugs, as reported for the uptake of TC by the same PA. This approach may be extremely useful if bentonite is not available, while PA reserves are in large quantity such as in arid regions, where water is also in scarcity.

References


