



Research paper

The adsorption of nortriptyline on montmorillonite, kaolinite and gibbsite

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ABSTRACT

Nortriptyline (NT) is a tricyclic antidepressant in common use in many countries. Its presence in drinking water indicates that current wastewater treatment practices fail to remove it effectively from effluents with consequent adverse effects on aquatic organisms. Since mineral surfaces readily remove many organic substances from effluent streams, this research sought to study the adsorption of NT on montmorillonite, kaolinite and gibbsite. Adsorption edge and isotherm experiments were performed to determine the relative effectiveness of the three substrates for NT removal, and X-ray diffraction (XRD) and attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy were used in order to gain an understanding of the mode of adsorption. Adsorption of NT on all three substrates was effectively independent of pH in the range from 3 to 12. Both montmorillonite and kaolinite proved to be excellent adsorbents of NT with maximum adsorption capacities of 19.3 and 6.4 $\mu\text{mol m}^{-2}$ respectively at pH 6.0, but gibbsite adsorbed relatively little. The XRD and ATR-FTIR results indicated that NT formed a multilayer on montmorillonite with no evidence of intercalation. Both electrostatic and hydrophobic interactions appeared to play important roles in the adsorption.

1. Introduction

Nortriptyline (NT) is a commonly prescribed tricyclic antidepressant (TCA) and is used in the clinical treatment of mood disorders such as depression and anxiety, as well as neuropathic pain (AMH, 2009). A number of studies on antidepressants have reported significant adverse effects on aquatic organisms (Brooks et al., 2003; Calisto and Esteves, 2009; Sanderson et al., 2003; van der Ven et al., 2006). Since TCAs are associated with the majority of deaths from antidepressant overdose (Thanacoody and Thomas, 2003), they are considered one of the most toxic substances affecting the central nervous system directly and thus disrupting neuro-endocrine signalling (Sanderson et al., 2003). The large quantity of TCA used over the past few decades has led to their widespread detection in surface water and bio-solids (Li et al., 2013). Pharmaceuticals not completely removed in wastewater treatment plants are often discharged, resulting in the contamination of streams, groundwater, and sometimes, drinking water. In 2008, alarming amounts of TCA were found in drinking water (Snyder, 2008), revealing the inefficiency of water treatment plants in removing these chemicals. The main concern with psychoactive products is not necessarily the high volume of a certain drug, but the environmental persistence and critical biological activity of both the drug, and their metabolites (Fent et al., 2006).

In wastewater treatment, adsorption to solid particles plays an

important role in the removal of pollutants. Both hydrophobic and electrostatic interactions between adsorbents and adsorbates have significant influence on adsorption (Hörsing et al., 2011). Clay minerals are one of the major materials used for the treatment of wastewater (Park et al., 2011), due to their high cation exchange capacity (CEC), and high specific surface areas (Adebajo et al., 2003). Both organic and inorganic pollutants can be removed rather efficiently via adsorption onto mineral surfaces (Park et al., 2011). Since clay minerals have a range of charged surface sites, including permanent negatively charged sites resulting from isomorphous substitution, and pH-dependent charged sites resulting from protonation or deprotonation of surface hydroxyl groups, a range of adsorption mechanisms is possible for ionic organic compounds (Sposito et al., 1999). In order for hydrophobic organic compounds to adsorb, adsorbents with higher hydrophobicity are needed. For ionisable substances solution pH plays an important role in their affinity to the solid surfaces (Adebajo et al., 2003). TCAs are organic bases containing amine groups. Generally compounds with higher pK_a values have been found to adsorb more readily to negatively-charged substrates like most clay minerals, as these compounds have a positive charge when the solution pH is below their pK_a (Gilchrist et al., 1993).

While previous work has been carried out on the persistence of TCAs in agricultural soils (Li et al., 2013), there has been limited research conducted on their adsorption behaviour. The important role of clay

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minerals affecting the release and transport of pharmaceutical compounds in environmental situations is reflected by the fact that clays are used extensively in pharmaceutical products to modify release and absorption profile (Carretero and Pozo, 2010). In addition, modified clays have been investigated by Radian et al. (2015) as a means of removing pharmaceuticals from contaminated water systems. Only recently the uptake of Amitriptyline (AT), another member of the TCA family, was investigated on kaolinite (Lv et al., 2013) and Ca-montmorillonite (Chang et al., 2014), two major soil mineral components. The uptake of AT on kaolinite was found to be very rapid, suggesting surface adsorption, instead of intercalation (Lv et al., 2013). However, for Ca-montmorillonite X-ray diffraction patterns showed a significant increase in the d-spacing and characteristic FTIR (Fourier transform infrared spectroscopy) band shifts toward higher wavelengths after AT adsorption, implied that the adsorbed drug molecules were intercalated into the interlayer of the mineral (Chang et al., 2014). Correlation between the desorbed cations and the concentration of the AT remaining in solution suggested cation exchange as the main adsorption mechanism in both kaolinite and Ca-montmorillonite (Chang et al., 2014; Lv et al., 2013). The adsorption of Doxepin, a relatively new member of the TCA family with a tertiary amine functional group (AMH, 2009), on a Na-montmorillonite was studied, and adsorption was found to be mainly driven by electrostatic interactions together with hydrophobic interactions (Thiebault et al., 2015).

The widespread use of TCAs over the past few decades, their increased detection in water supplies (Calisto and Esteves, 2009), as well as their high persistence in the environment and toxicity to non-target organisms (Snyder, 2008), justify the growing concern about these pollutants and the need to study their fate in the environment. The goal of this research was to study the interactions between NT and three minerals, Na-montmorillonite, kaolinite and gibbsite, with diverse properties, including specific surface area, cation exchange capacity (CEC), and hydrophobic content. Experiments studying the effect of pH and concentration of NT, together with XRD and ATR-FTIR measurements, aimed to understand the mechanism of NT removal by these substrates.

2. Materials and methods

2.1. Reagents

All solutions used in these experiments were prepared with Milli-Q water (Millipore, Bedford USA). NT or [3-(10, 11-dihydro-5H-dibenzo [a, d] cyclohepten-5-ylidene)-N-methyl-1-propanamine] in an HCl form, was purchased from Sigma–Aldrich, Australia. It has a molar mass of 299.84 g mol⁻¹ and its pK_a value is 9.7 (Clarke, 1975). Its chemical structure is illustrated in Fig. 1. All other chemicals were of analytical reagent grade.

2.2. Adsorbent

The clay samples were obtained from the Clay Mineral Society Source Clays Repository, with Na-montmorillonite (SWy-3) from Wyoming, USA, and kaolinite (KGa-2) from Warren County, Georgia. Both minerals were used without further treatment. The specific surface

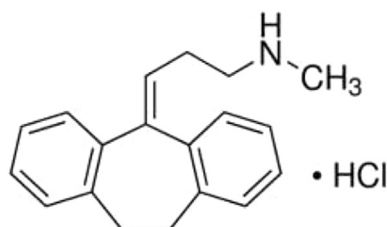


Fig. 1. The chemical structure of Nortriptyline HCl.

areas of the Na-montmorillonite and kaolinite were 31.82 m² g⁻¹ and 23.5 m² g⁻¹ respectively (Clay Minerals Society, 2018).

Gibbsite was prepared using the same synthesis method detailed by Ruyter-Hooley et al. (2016). The BET surface area of the gibbsite powder was found to be 44.1 m² g⁻¹ (Ruyter-Hooley et al., 2016). The pH_{PZC} for gibbsite prepared by this method has been determined to be 9.0 (Rosenqvist et al., 2002).

2.3. Equipment

All experiments were conducted in air-tight borosilicate glass water-jacketed reaction vessels with a total volume of about 400 mL. Water, maintained at 25 °C, was circulated through the water jacket of the reaction vessel by use of a Haake K15 circulator to maintain a constant temperature during experiments. The suspensions were stirred continuously with a magnetic stirrer and pH measurements were performed using an Orion Sureflow pH electrode coupled to a Metrohm model 691 pH meter. pH adjustments were made with either HCl or NaOH solution while the pH electrode was calibrated at the reaction temperature before each experiment using 0.05 M potassium hydrogen phthalate and 0.025 M phosphate buffers.

2.4. Adsorption experiments

Adsorption experiments were carried out in duplicate with all experimental data shown in the accompanying figures. Preliminary kinetic experiments indicated that the adsorption process was complete within 10 min; hence all experiments were left for 30 min to reach equilibrium.

For adsorption edge experiments, sufficient of the chosen mineral to provide a surface area of 100 m² L⁻¹ was added to a glass reaction vessel containing 1 mM NaCl, and stirred for at least 12 h to equilibrate. The pH of the equilibrated mineral dispersion was adjusted to 3.5 with HCl and a NT aliquot added to provide a concentration of 0.10 mM. The pH was readjusted to 3.5 and the dispersion left for 30 min to reach equilibrium. A 3 mL sample was taken with a disposable syringe and filtered using 25 mm Whatman 0.22 μm Glass Microfiber filter paper. The pH of the remaining dispersion was then increased by approximately 1.0 unit, left for 30 min to equilibrate, and another 3 mL sample taken and filtered. This process was repeated until 10 samples were obtained over the pH range from 3 to 12. The NT concentration of each filtered dispersion sample was determined with a High Performance Liquid Chromatograph (HPLC, Agilent 1220 infinity LC) equipped with a Phenomenex C18 reverse phase column (Kinetex 2.6 μm, 100 × 2.1 mm) and a diode array UV–vis detector at a wavelength of 240 nm. The mobile phase consisted of 60% (v/v) acetonitrile in 25 mM phosphate buffer with a final pH of 7; the flow rate was 1.5 mL min⁻¹.

Isotherm experiments were conducted at pH 6 following a similar procedure to that used for the adsorption edge experiments. Sufficient of the chosen mineral to provide a surface area of 100 m² L⁻¹ was added to a glass reaction vessel, containing 1 mM NaCl, the pH adjusted to 6.0, and the dispersion stirred for at least 12 h to equilibrate. A NT aliquot was added to the equilibrated mineral dispersion to provide an initial solution concentration of 50.0 μM. The pH was re-adjusted to 6.0 and left for 30 min to reach equilibrium. A 3 mL sample was taken and filtered into a HPLC vial. Another NT aliquot was then added, the pH adjusted, and the process repeated until 10 samples were obtained with the total amount of NT the range from 15 mmol to 375 mmol. NT concentrations of the filtered dispersions were determined using HPLC.

2.5. FTIR spectroscopy

ATR-FTIR spectra were collected for the NT-SWy-3 system. All spectra were measured using a Bruker Equinox 55 FT-IR spectrometer equipped with a SensIR Technologies DurasampIR horizontal ATR attachment incorporating a diamond coated, 9-bounce ZnSe ATR crystal.

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