



Contrasting mechanisms of metoprolol uptake on kaolinite and talc



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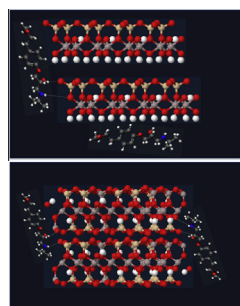
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HIGHLIGHTS

- Uptake of metoprolol (MT), a beta-blocker, on different clays was studied.
- Electrostatic interactions influenced mainly for MT uptake on kaolinite.
- Hydrogen bonding and hydrophobic interactions affected MT uptake on talc.

GRAPHICAL ABSTRACT

Interactions between MT and kaolinite (top) and talc (bottom). Hydrogen donor bonding by MT was indicated by white dashed lines while hydrogen acceptor bonding by green dashed lines that are missing for MT uptake on talc due to lack of hydroxyl group on the external surfaces.



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ABSTRACT

Due to their widespread use and limited human metabolism, β -blockers were widely detected in sewage effluents and surface waters. β -blockers are persistent in agricultural soils that have been irrigated with treated wastewater or fertilized with sewage sludge. It is important to study β -blockers interaction with kaolinite and talc because kaolinite is a major component of soil that formed under warm and humid conditions, and talc is frequently used as an excipient for drug formulation. In this study, the interactions between metoprolol (MT), a β -blocker, and kaolinite and talc, clay minerals of 1:1 and 2:1 structural types, were investigated under varying physical and chemical conditions. Uptake of MT on both minerals was instantaneous with capacities close to the cation exchange capacity of the substrates. MT sorption was exothermic and the free energy of sorption was small and negative. These parameters pointed out to physical sorption for the uptake of MT on these minerals. Both solution pH and ionic strength had significant effects on MT uptake on kaolinite, but minimal influence on talc, contrasting different mechanisms of MT uptake on these minerals. The FTIR results showed bands blue shifted for both in-plane and out-of-plane bending of NH_2 . Meanwhile, blue shift was also found for the 1246 and 1011 cm^{-1} bands, attributed to aromatic ether, after MT sorption on kaolinite and talc. For talc, blue shift of the band at 965 cm^{-1} , attributed to aliphatic ether, was also observed. These results suggested that electrostatic interactions or hydrogen bonding played important roles in MT uptake on kaolinite. In contrast, the hydrogen bonding and hydrophobic interaction were likely the main mechanisms of MT uptake on talc.

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1. Introduction

Beta-blockers (β -adrenergic receptor antagonists) are a class of widely prescribed cardiovascular drugs, used for the treatment of hypertension, cardiac arrhythmias, cardio protection after heart attacks, and anxiety disorders [2]. Due to their widespread use, limited human metabolism, and lower removal rate, β -blockers are widely detected in sewage effluents and surface water [19] and are persistent in agricultural soils after irrigation with treated wastewater [15]. As such, significantly higher concentrations of metoprolol (MT), one of the commonly prescribed β -blockers, were found in the leaves of plants grown in soils containing a low level of soil organic matter and clay (i.e., sandy and aeolian soils) since MT was most likely loosely bound to the negatively charged clay minerals and organic matter [13]. Toxicological data from a green algae test (*Scenedesmus vacuolatus*) suggested that propranolol and MT could be considered harmful to aquatic organisms, however, their sorption on solids may explicitly inhibit the hazardous effects [29].

In both wastewater influent and effluent in several Spain wastewater treatment plants (WWTPs) the frequency of its detection was as high as 89% [14]. Even more, a 97% detection of MT was found in both the influent and effluent from 30 samples collected in 14 WWTPs [11]. Although the global removal rate of MT in 12 conventional WWTPs ranged from –40% to 100% with a mean of 40% [11], a net removal rate as low as 6% was reported from a WWTP in Seoul [31].

The higher frequency of detection of β -blockers was attributed to their higher stability, lower removal rate, and non-biodegradable nature. In a hydrolytic stability test, MT was found stable under pH 4, 7, and 9, with an estimated half-life of more than a year in aquatic environments at 25 °C [28]. Laboratory measurements of direct photolysis of MT resulted in a $t_{1/2}$ of 630 and 990 h with initial MT concentrations of 1 and 10 mg/L [24]. No biodegradation was detected over a 50 pore-volume time span in a column transport experiment with an input MT concentration of 0.5 mg/L [41], nor in the nitrification enrichment culture [40].

Abiotic processes were the sole process responsible for the overall MT removal among which sorption was an important one; as demonstrated in a field scale study along a 16.2 km stretch of Sáva Brook [38]. However, conflicting results were reported on MT sorption on solids. Powder activated carbon was able to remove >90% MT by adsorption from the effluent of a Berlin WWTP with a concentration of 2.4 $\mu\text{g/L}$ [39]. Both ionic and hydrophobic interactions played important roles for the adsorption of β -blockers on charcoal [42]. On the contrary, the estimated solute distribution coefficient K_d value of MT was about 0 L/kg [6], indicating no adsorption of MT on solid surfaces.

Clay minerals are major soil components that have large surface area (SA) and high cation exchange capacity (CEC). In this study, we choose kaolinite, a common soil mineral found in warm and humid regions, and talc, a commonly used excipient, to study their interactions with MT. Together with our previous studies [17,21] on interactions between atenolol (AT), another commonly prescribed β -blocker, and kaolinite and talc, we anticipate to shed some light on elucidating mechanisms of interactions between clay minerals and β -blockers in the environment.

2. Materials and methods

Metoprolol (CAS # 37350-58-6), 1-[4-(2-methoxyethyl)phenoxy]-3-[(1-methylethyl)amino]-2-propanol (Fig. 1) has a molecular weight of 267.364 g/mol and a pK_a of 9.2 [2] or 9.6 [32]. However, two MT molecules are balanced by the anion tartrate in a crystalline form, resulting in a formula of

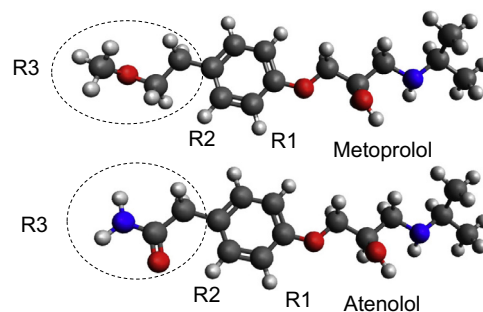


Fig. 1. Molecular structure of metoprolol and atenolol. The red is O, the blue is N, the dark gray is C while the white is H. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

($\text{C}_{15}\text{H}_{25}\text{NO}_3$) $_2 \cdot \text{C}_4\text{H}_6\text{O}_6$ and a formula mass of 684.82 g/mol with a CAS # 56392-17-7. The $\log K_{\text{OW}}$ values for neutral and cationic species were 1.95 and –1.10, respectively [41]. An experimental and predicted solubility of $\log S_0 = -1.2$ and –2.3, corresponding to 17 and 1.3 g/L, was reported [16].

The kaolinite used (KGa-2) is a poorly crystallized kaolinite obtained from the Clay Mineral Repository in Purdue University. It has a CEC value of 37 mmol/kg [4] and an SA of 21.7 m^2/g [10]. Na^+ , Ca^{2+} , and Mg^{2+} are the major exchangeable cations of kaolinite. The point of zero charge (pzc) of the kaolinite determined from potentiometric titration was 4.0 [23]. The talc used was purchased from Acros. It has an SA of 2.3 m^2/g . Due to its low isomorphous substitution in tetrahedral and octahedral sites, talc has essentially no permanent surface charges [3]. Its extremely low CEC was originated from its pH dependent surface charges. The isoelectric point was located around pH 2.5 [44]. Both minerals were used without further pre-treatment.

In all batch experiments, 1.0 g of mineral was combined with 10 mL of MT aqueous solution in 50 mL centrifuge tubes, and duplicate samples per experimental condition were tested. The initial MT concentrations were 0–4 mmol/L for the isotherm study and 1 mmol/L for all other tests. Samples were shaken at 150 rpm for 24 h, with the exception of the kinetic study. The mixtures were then centrifuged at 3500 rpm for 10 min, and the supernatants were passed through 0.45 μm syringe filters before being analyzed for the equilibrium MT concentrations using an UV–Vis method. The pH of the supernatant was measured, but no pH adjustment was made except the pH study. In the kinetic experiment, the samples were shaken for 24, 8, 4, 2, 1, 0.5, and 0.25 h. For the pH study, the equilibrium solution pH was maintained at 2–11 with an increment of 1, adjusted by periodically adding minute amounts of 1 M HCl or NaOH. While 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 isosbestic point was reported at 264 nm [36]. However, for UV–Vis analysis, 274 nm was one of the absorbance maxima [25] and was used in many studies [5,9,12,34,36,42] thus, it was also used in this study. The FTIR analysis was conducted using a Jasco FT/IR-4100 Spectrometer equipped with a ZnSe crystal and Attenuated Total Reflection accessory. The spectra were obtained from 600 to 4000 cm^{-1} by accumulating 256 scans at a resolution 4 cm^{-1} . The powder X-ray diffraction (XRD) analyses were carried out using a D8 ADVANCE diffractometer (Bruker Corp.) under a $\text{CuK}\alpha$ radiation at 40 kV and 40 mA. Samples were scanned from 2° to 40° 2θ with a scanning speed of 0.01°/s.

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