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Modeling and site energy distribution analysis of levofloxacin sorption by biosorbents

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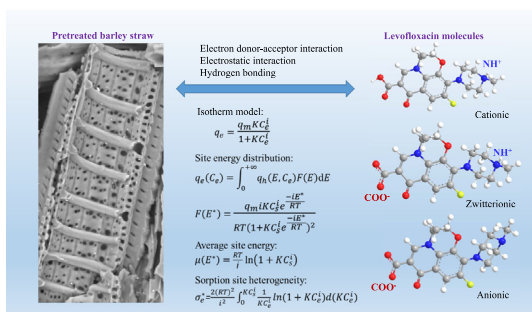
HIGHLIGHTS

- An adsorption equilibrium model was applied to well simulate the sorption of levofloxacin.
- The biosorbent demonstrated high capacity of levofloxacin sorption at various pH.
- Approximate site energy distribution of the sorption system was determined.
- Levofloxacin sorption was through multiple adsorption mechanisms.
- Desorption efficiencies of the loaded levofloxacin indicated the strong binding.

GRAPHICAL ABSTRACT



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ABSTRACT

An adsorption equilibrium model was applied to simulate the sorption of an antibiotic, levofloxacin (LEV), one of the emerging contaminants, from aqueous solution by the biosorbent based on pretreated barley straw. The effects of solution pH, contact time, LEV concentration and ionic strength on LEV removal were investigated, and desorption of LEV loaded on pretreated barley straw was also examined. In addition, site energy distribution of the pretreated biosorbent for LEV molecules adsorption was estimated. The average site energy and standard deviation of the site energy distribution under various pH values were determined and applied to analyze the interaction between the biosorbent and adsorbate, and sorption site heterogeneity. With higher average site energy (28.1 kJ/mol), the pretreated barley straw at neutral pH had higher sorption affinity, thus be more favorable for the sorption reaction than the lower affinity surface at acidic or basic pH. The experimentally achieved LEV uptake of the pretreated barley straw at pH 6.88 is much higher than that of raw barley straw, and other sorbents reported in literatures. The methods of biomass pretreatment and site energy distribution analysis could be transferable to extended organics or inorganics adsorption by biosorbents.

1. Introduction

Fluoroquinolones (FQs) are the newest class of antibiotics and a class of broad spectrum antibiotics that are commonly used in both human and veterinary medicine. FQs in the environment are of concern because they are widely used but not readily biodegradable by microorganisms [1,2]. The total annual consumption of

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Nomenclature

[A]	equilibrium adsorbate concentration (mmol/L)
$[A_iB]$	occupied binding sites on a heterogeneous adsorbent (mmol/g)
[B]	unoccupied binding sites on a heterogeneous adsorbent (mmol/g)
A	adsorbate
B	binding site on a heterogeneous adsorbent
C_e	equilibrium adsorbate concentration (mol/L or mg/L)
C_s	maximum solubility of solute in water (mol/L or mg/L)
E	sorption energy refers to the difference between the solute and solvent (water) for a given sorption site (kJ/mol)
E^*	difference of sorption energy at C_e and C_s (kJ/mol)
E_s	value of the sorption energy corresponding to $C_e = C_s$ (kJ/mol)
$F(E)$	site energy frequency distribution over a range of energies
$F(E^*)$	site energy distribution over a range of energies (mg·mol/(g·kJ))
i	the estimated number of adsorbate molecules which share the same adsorption site dependent on solution pH
K	adsorption constant ($(\text{mmol/L})^{-i}$)
q_e	equilibrium binding capability of an adsorbate with benzene rings (mmol/g or mg/g)
q_h	energetically homogeneous isotherm (mmol/g)
q_m	maximum binding capability of an adsorbate with benzene rings (mmol/g or mg/g)
R	gas constant (8.314 J/(mol·K))
R^2	coefficient of determination
RSS	residual sum of squares ($(\text{mmol/g})^2$)
T	temperature (K)

Abbreviations

EDA	electron donor-acceptor
FTIR	Fourier transform infrared spectroscopy
HPLC	high performance liquid chromatography
LEV	levofloxacin
PBS	pretreated barley straw
PZNC	point of zero net charge
RBS	raw barley straw

the human antibiotic FQs in USA was 277.44 tons for the year of 2011 reported by Food and Drug Administration [3]. Among the FQs, levofloxacin (LEV) is a new kind but already widely used antibiotic, which acts by inhibiting bacterial DNA gyrase enzyme required for DNA replication [4]. Fig. 1 shows molecule structure and the charge state of LEV [5]. In 2011, more than 55 tons of LEV were used for human in USA, and it ranked second in the FQs consumption [3]. However, LEV is not completely metabolized in humans and animals, and it cannot be completely removed during wastewater treatment using current technologies, and eventually it is discharged into the environment. It may present a risk to human health through contaminated drinking water.

Adsorption is one of the most effective methods for removing pollutants from water. However, studies involving the use of low cost biomass for removal of pharmaceutical contaminants from effluents are still scarce in literatures. In previous research, barley straw, an abundantly generated agricultural byproduct, has been used for biosorption of nickel from simulated wastewater and

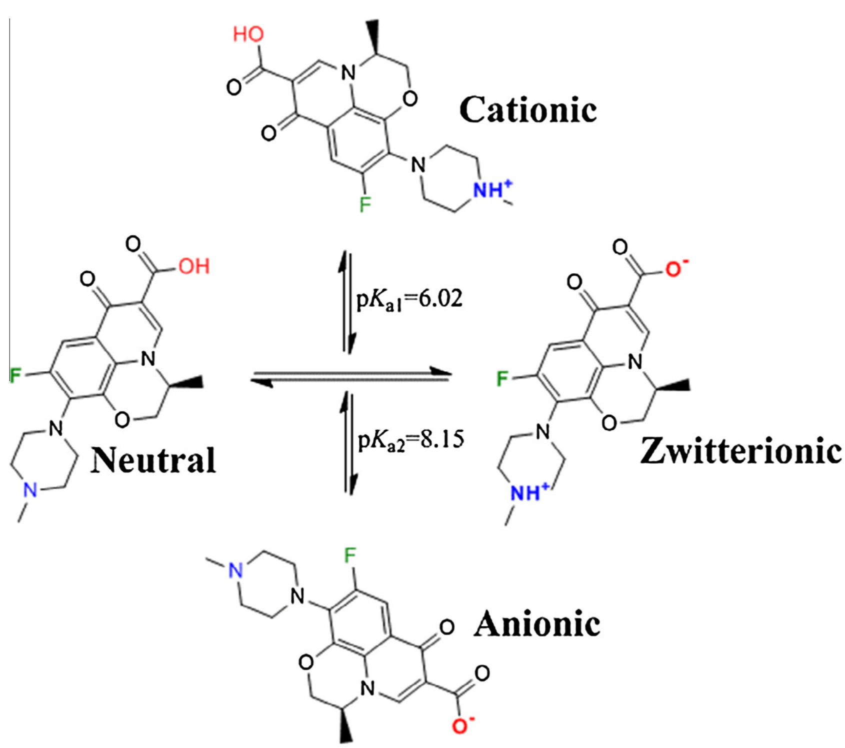

Fig. 1. Molecular structure and pH-dependent speciation of LEV.