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Modification of biochar derived from sawdust and its application in removal of tetracycline and copper from aqueous solution: Adsorption mechanism and modelling

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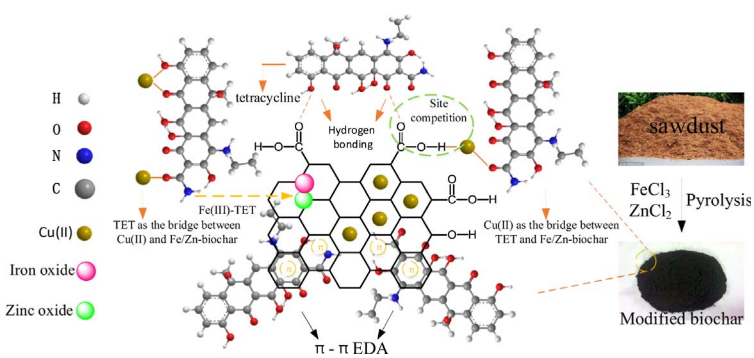
GRAPHICAL ABSTRACT



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ABSTRACT

Highly efficient simultaneous removal of Cu(II) and tetracycline (TET) from aqueous solution was accomplished by iron and zinc doped sawdust biochar (Fe/Zn-biochar). The mutual effects and inner mechanisms of their adsorption onto Fe/Zn-biochar were systematically investigated via sole and binary systems, sorption isotherm and adsorption kinetics models. The liquid-film diffusion step might be the rate-limiting step for tetracycline, the interaction of Cu(II) was more likely controlled by both intra particle diffusion model and liquid film diffusion model. The fitting of experimental data with kinetic models, Temkin model indicates that the adsorption process of tetracycline and Cu(II) involve chemisorption, and physico-chemical adsorption, respectively. There exists site competition and enhancement of Cu(II) and tetracycline on the sorption to Fe/Zn-biochar. The results of this study indicate that modification of biochar derived from sawdust shows great potential for simultaneous removal of Cu(II) and tetracycline from co-contaminated water.

1. Introduction

Antibiotics are emerging pollutants of particular concern because of their widespread use in animal and human medicine (Norvill et al., 2017). Tetracycline (TET), a common antibiotic, has been widely used in the agriculture and livestock industry, and 60–90% of the parent

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compound is discharged into aquatic environments in original and metabolized forms because of the incomplete metabolism of TET by animals (Zhu et al., 2014). Selvam et al. analyzed the influence of livestock activities on the concentrations of TET in Yuen Long, Kam Tin, and Shing Mun rivers of Hong Kong, concluding that TET were at the concentration range of 30–497 ng/L (Selvam et al. (2017)). Copper (Cu) is also widely used in livestock and poultry industry as feed additives due to its growth-promoting effect (Ostermann et al., 2015). Ji and coworkers reported that the concentrations of Cu(II) and TET in animal manures (i.e., dry swine, poultry and cattle manures) in Shanghai, China were at the range of 32.3–730.1 mg/kg and 4.54–24.66 mg/kg, respectively (Ji et al., 2012). Obviously, Cu(II) and TET could easily form complexes, and the waterbody and soil environment nearby livestock farms are contaminated by both of them (Wang et al., 2016b).

In addition, antibiotics like TET could induce the generation of antibiotic-resistant genes (ARGs) in microorganisms (Wang et al., 2017b), which can proliferate and widely disseminate in ecosystems, thereby posing a great danger to human health (Huang et al., 2016b). Furthermore, the presence of heavy metals, especially, Cu(II) has been shown to increased occurrence of ARGs even at relatively low levels, thus elevating the health risk (Poole, 2017). The co-existence of Cu(II) and TET occur as complex solute mixtures in contaminated water and soil, and pose more serious toxicological problems to the environment because of their relative mobility and combined toxicity. Therefore, it is necessary to develop integrated techniques realizing the removal of Cu (II) and TET simultaneously.

There are several methods (e.g., adsorption, advanced oxidation, electrochemical methods, biological treatment) that have been extensively applied to remove antibiotics and/or heavy metals (Ahmed et al., 2017; Chen et al., 2017; Liu et al., 2017). Among these methods, the adsorption technology was a priority choice because of a synthetic consideration of removal efficiency, simplicity, safety and economic feasibility in the treatment process (Yu et al., 2017). Furthermore, various adsorbents such as functionalized carbon nanotubes (Li et al., 2014), graphene-based materials (Huang et al., 2016a), polystyrene-divinylbenzene resin (Ling et al., 2016), biosorbents (Wang and Chen, 2014) and etc. have been applied to remove the coexisting pollutants of antibiotics and/or heavy metals with a positive effect in aqueous solution previously.

Moreover, searching for new efficient, simple and inexpensive method to control heavy metals and antibiotics is also of considerable interest. Nowadays, biochar-based materials have been extensively studied and widely applied in the environmental remediation because of its inherent characteristics: (i) biochar is cheap, non-toxic and easy to obtain, (ii) biochar possess intrinsic high specific surface areas, large pore volumes, enabling the possibility of physisorption and hydrophobic interaction and electrostatic adsorption with pollutants efficiently, (iii) biochar can be modified briefly and possess an increasing number of oxygen containing functional groups on biochar's surface, which enabling the possibility of specific binding (e.g., hydrogen bonding, π-π electron-donor–acceptor interactions as well as covalent binding) for contaminants efficiently (Mohan et al., 2014; Wang et al., 2017a). Hence, to enhance the adsorption effect of pristine biochar, the modification of biochar was essential to improve its surface properties (e.g., surface area, pore volume, hydrophobic/hydrophilic property, or surface charge). And the most popular reagents which are used for functionalization of biochar surface include nanoscale zerovalent iron (Dong et al., 2017), bimetallic layered double hydroxide (e.g., Mg/Al, Ni/Mn, Mg/Fe) (Tan et al., 2016b; Wan et al., 2017), amino groups (Ma et al., 2014a), oxygen-containing functional groups (Huang et al., 2015). Results suggest that functionalization of raw biochar could toward dramatically improve its adsorption ability. For examples, Wang et al. and Liang et al. used manganese oxide-modified biochar composites for the sorption of As(V), Pb(II) and Cd(II) with highly sorption capacity because of the strong As(V), Pb(II) and Cd(II) affinity of its birnessite particles (Liang et al., 2017; Wang et al., 2015). Tan and coworkers reported Na_2S modified biochar enhanced the sorption capacity for Hg(II) because of carboxyl, hydroxyl groups and sulfur impregnation on the sorbents contributed to Hg(II) sorption (Tan et al., 2016a).

Recently, zinc-biochar (Gan et al., 2015), iron-biochar (Peng et al., 2014; Wu et al., 2016; Zhou et al., 2017c) and iron/zinc-biochar (Wang et al., 2016a) were synthesized in laboratory, and used for the effective removal of heavy metals and recalcitrant organic compounds from wastewater. Previous works indicated that the surface and physicochemical properties of biochar can be easily modified with functional groups or incorporated with zinc and/or iron, exhibiting improved physical or chemical properties for the removal of hazardous contaminants.

Hence, on the basis of previous works, the purposes of this research were to (1) study the adsorption ability of the prepared iron and zinc doped sawdust biochar (Fe/Zn-biochar) for tetracycline and Cu(II) simultaneously, (2) investigate the impacts of some key parameters, namely pH, and contact time on the adsorption capacity, (3) explore the modelling of adsorption isotherms and kinetics to help explain its adsorption mechanism of Cu(II) or tetracycline, (4) investigate the underlying mechanisms of tetracycline and Cu(II) adsorption onto Fe/Zn-biochar. This study provides new insights in the development of biochar-based materials and advances their applications in water treatment.

2. Materials and methods

2.1. Materials and chemicals, and preparation of biochar based-materials

The used materials and chemicals are presented in supporting information. The preparation procedure of pristine biochar (P-biochar), Zn-biochar, Fe-biochar and Fe/Zn-biochar were prepared according to the strategy reported previously (Wang et al., 2016a). Typically, the mixture of sawdust (15 g) and the solution containing $ZnCl_2$ (0.2354 g), $FeCl_3 \cdot 6H_2O$ (0.72321 g) and a certain volume of water was stirred for 24 h, then kept at 100 °C. The aqueous solution containing $ZnCl_2$ and $FeCl_3 \cdot 6H_2O$ was repeatedly added to the above sample, and treated as described above to increase the iron and zinc oxide loading amount. Finally, the pretreated sawdust was calcined at 600 °C for 2 h with a heating rate of 5 °C/min in the tube furnace under nitrogen flow. For comparison, Fe-biochar, Zn-biochar and P-biochar were prepared by the same method.

The batch adsorption studies were presented in supporting information. The zeta potential of biochar based-materials was determined by using Electroacoustic Spectrometer (ZEN3600 Zetasizer UK) at varying solution pH from 2.0 to 9.0, and the result was presented in supporting information. Furthermore, the structural information of SEM for P-biochar Zn-biochar, Fe-biochar and Fe/Zn-biochar was presented in supporting information. The N_2 sorption isotherms with the corresponding pore distribution curves, X-ray powder diffraction (XRD), Fourier-transform infrared (FT-IR) spectrum, and magnetic data were described in previous work, indicating that the Fe/Zn-biochar was enriched with oxygen-containing functional groups, and enhanced with surface area, pore volume and average pore (Wang et al., 2016a). The oxygen-containing functional group and increased surface area, pore volume and average pore on the outside of the Fe/Zn-biochar implied it contained both hydrophilic and hydrophobic sites (Wang et al., 2016a).

2.2. Experimental data modeling

Six kinetic models: the pseudo-first-order, pseudo-second-order, elovich, two-compartment first-order equations, intra-particle diffusion and liquid film diffusion were used to test experimental data to examine the adsorption kinetics (Zhou et al., 2017a; Xiong et al., 2017), the equations were presented as follows:

(a) Non-linear pseudo-first-order: