Effect of Cu(II) on adsorption of tetracycline by natural zeolite: performance and mechanism
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ABSTRACT

The purpose of this study was to investigate the effect of Cu(II) on the adsorption performance and mechanism of tetracycline (TC) adsorption by natural zeolite (NZ) in aqueous solution. Low levels of Cu(II) (<0.01 mmol/L) enhanced the extent of TC adsorption from ∼0.4 mg/g (in the absence of Cu(II)) to ∼0.5 mg/g (with 0.01 mmol/L Cu(II)), resulting in 99% removal of the total TC content. The TC adsorption gradually decreased with increase in the initial pH, but the coexistence of Cu(II) lowered the extent of decrease. The adsorption process was better simulated by the pseudo-second-order kinetics model, but the isotherm model that was more fitting changed from the Langmuir to the Freundlich model as Cu(II) increased, indicating the coexistence of Cu(II) and TC altered the adsorption mechanisms. However, the residual TC in solution increased from 0 to ∼6 mg/L as the concentration of Cu(II) increased from 0 to 1 mmol/L, suggesting a competition between TC and Cu(II) for the adsorption sites in NZ. Fourier transform infrared spectroscopy analysis showed that the functional groups on the surface of NZ changed after the adsorption of TC, suggesting that complex reactions had occurred on the surface of the adsorbent.

INTRODUCTION

Antibiotics are mainly used to treat and prevent infectious disease in humans and animals (Tran et al. 2016; Le et al. 2018). The major portion of consumed antibiotics is excreted to the environment from hospitals, industrial wastewater, urine, and feces (Binh et al. 2018; Tran et al. 2018). Recently, antibiotics pollution in the environment has caused severe concerns, as antibiotics cannot be easily metabolized by animals and are not easily biodegradable, leading to their persistence in the environment (Chen et al. 2017; Karpov et al. 2018). One of the major concerns regarding antibiotics is the evolution of antibiotic resistant bacteria and antibiotic resistant genes (Tran et al. 2016; Yi et al. 2017; Le et al. 2018). Among the various antibiotics, tetracyclines (TCs) are one of the commonly used antibiotics for livestock and aquaculture (Bush & Bradford 2016; Tran et al. 2018). The concentrations of TCs in raw influent and sewage sludge and biosolids from full-scale wastewater treatment plants (WWTPs) ranged from a value below the method quantification limit to 48,000 ng/L in different geographical regions (Tran et al. 2018). They cannot be completely removed by the WWTPs, and efficient methods for their removal are urgently needed.

Heavy metals, such as copper (Cu), are widely used as animal feed additions to control diseases and promote animal growth (Jia et al. 2016). The Cu contents in dairy feed and manure are 127 and 66.68 mg/kg in China, respectively (Li et al. 2019), and the amount of Cu entering the WWTPs ranged from 5% to 59% of the total load into WWTPs in EU countries (Cantinho et al. 2016). Cu can undergo a complexation reaction with several groups of antibiotics, including NH₂ group, aromatic ring, OH group, and C=O group (Mondal et al. 2016; Singuru et al. 2016; Amaniampong et al. 2018b). The complexation of the two compounds causes detrimental effects such as the inhibition of enzyme and microbial activity, antagonistic effect on plants, and the production of antibiotic and heavy metal cross-resistance genes in microorganisms (Wang et al. 2019; Zhou et al. 2019). Thus, it is of great importance to develop effective and low-cost technologies for the removal of both antibiotics and Cu-combined antibiotics from water.

Among the several treatment methods (e.g., biological treatment (Wang et al. 2019), bioelectrochemical treatment...
systems (Yan et al. 2019), photocatalysis (Wang et al. 2018a) etc.) for removing antibiotics and/or heavy metals, adsorption is a simple, economical, and efficient method. Various materials, such as nanosilica (Pham et al. 2018) and biochar (Zeng et al. 2013; Zhou et al. 2019), have been used as adsorbents for the removal of antibiotics and Cu. Despite the efficient removal performance obtained in these studies, real world applications of these adsorbents are limited due to high costs and the difficulty of regenerating the adsorbent.

Compared with synthetic materials, natural materials are cheaper and easier to obtain, and thus may be more suitable for the antibiotic adsorption. In particular, natural zeolite (NZ), which is hydrated aluminosilicate material that exists in the lithosphere of the crust, can be easily obtained naturally (Li et al. 2018; Sousa et al. 2018). Previous studies have provided some insight into the antibiotic-removal process using zeolites, and satisfactory removal rates were obtained (Ali & Ahmed 2017; Peng et al. 2018). In terms of removing Cu, zeolite has also proved to be an efficient adsorbent (Liu et al. 2019). However, few studies are focused on the Cu-influenced adsorption of TC by NZ. In addition, the study of adsorption of TCs by natural and synthesized zeolites found inconclusive results. For example, Ali et al. (2018) and Lye et al. (2017) believed that TCs adsorption on zeolites mainly involved electrostatic interaction between positively charged TCs and negatively charged zeolites. An et al. (2015) argued that sorption of TCs on modified zeolite may involve electrostatic attraction and cation exchange, whereas Guo et al. (2017) reported that adsorption mechanisms of TCs onto modified zeolite were dependent on multiple interactions including hydrophobicity, ion exchange, and surface complexes. Considering the variations in zeolite samples and experimental conditions, it is unsurprising that these reports present conflicting data. Thus, the underlying mechanism of TCs adsorption by NZ affected by Cu(II) is still unclear, and merits further research.

Typical TCs include tetracycline (TC), oxytetracycline, and chlorotetracycline, which have similar structures (Table S1, available with the online version of this paper). Here, TC was chosen as the target substance. The objectives of this study were to: (i) evaluate the effect of Cu(II) on TC adsorption by NZ; (ii) explore TC adsorption behaviors on NZ, including kinetics and adsorption isotherms studies, and the impacts of contact time, pH, and potential competitive adsorption between TC and Cu(II); (iii) investigate the mechanisms of TC adsorption and characterization of functional groups of NZ associated with TC and Cu adsorption.

MATERIALS AND METHODS

Materials

Hydrochloride salt of TC (purity >99%) was purchased from Dr. Ehrenstorfer GmbH (Germany) and stored at −20 °C. HCl, NaOH, and CuSO₄·5H₂O reagents (of analytical grade) were obtained from Sinopharm Chemical Reagent Co. (Shanghai, China). All solutions were prepared using 18 MΩ deionized H₂O at neutral pH (Millipore, USA).

NZ (diameter 5–8 mm, density = 0.80 g/cm³, porosity = 57%, Brunauer–Emmett–Teller surface area = 13.972 m²/g) was obtained from Kaibiyuan Co., Ltd in Beijing, China. NZ was first washed with deionized water three times and then oven-dried for 12 h at 80 °C, before cooling to room temperature.

Adsorption experiments

All batch adsorption experiments were conducted at 25 °C. A series of 1.5 L adsorption columns were used, in which NZ, TC, and Cu(II) were dissolved in 1 L aqueous solution. A peristaltic pump was set up to ensure that the aqueous solution circulated continuously; the circulation flow rate was maintained at 50 mL/min to ensure adequate contact between the adsorbates and adsorbents.

Effect of Cu(II) concentration on TC adsorption and adsorption kinetics

The effects of contact time (kinetics study) and Cu(II) concentration on TC adsorption by NZ was conducted as follows. To evaluate the adsorption potential and capacity of NZ, the initial concentrations were set high, in order to distinguish the adsorption performance under different conditions. A series of 1.5 L adsorption columns were filled with 40 g of adsorbent and 20 mg/L TC with 1 L of aqueous solution. The initial concentrations of Cu(II) in each aqueous solution ranged from 0 to 0.1 mmol/L. The initial pH of the solution was not adjusted. Samples were periodically withdrawn (0, 0.08, 0.25, 0.5, 1, 2, 4, 8, 12, 18, and 24 h) to determine the residual concentrations of TC in the solution. The calculation of the adsorbed amount and the kinetic models are given in the supplementary information (available with the online version of this paper).

Effect of initial solution pH on TC adsorption

The effect of solution pH on TC adsorption was investigated as follows: 40 g of adsorbent, 20 mg/L TC and 0–0.1 mmol/L
Cu(II) were mixed with 1.0 L aqueous solution in a series of 1.5 L adsorption columns. The solution pH was varied in the range of 2.0–10.0 using 0.1 mol/L HCl or 0.1 mol/L NaOH solutions. Samples were collected after 24 h to determine the residual concentrations of TC in the solution.

**Adsorption isotherms**

For the adsorption isotherm experiments, 40 g of adsorbent was placed in a series of 1.5 L adsorption columns, into which 1.0 L of adsorbate solution with varying initial concentrations (0–100 mg/L) was added, with 0–0.1 mmol Cu(II). The initial pH of the solution was not adjusted. Samples were collected after 24 h to determine the residual concentrations of TC in the solution. The Langmuir and Freundlich adsorption models were used to describe the adsorption equilibrium (supplementary information).

**Potential competitive adsorption of TC and Cu(II) on natural zeolite**

The potential competitive adsorption of TC and Cu(II) on NZ was investigated as follows. For the effect of Cu(II) addition on TC adsorption, a series of 1.5 L adsorption columns were filled with 40 g of adsorbent and 20 mg/L TC with 1 L of aqueous solution. The initial concentrations of Cu(II) in each aqueous solution ranged from 0 to 0.1 mmol/L. The solutions were filtered after 24 h and analyzed for the remaining concentration of TC.

For the effect of TC addition on Cu(II) adsorption, a series of 1.5 L adsorption columns were filled with 40 g of adsorbent and 0.1 mmol/L Cu(II) with 1 L of aqueous solution. The initial TC concentration in each aqueous solution ranged from 0 to 100 mg/L. The solutions were filtered after 24 h and analyzed for the remaining concentration of Cu(II).

**Analytical methods**

NZ was analyzed using scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX) (Inspect S50 model, FEI/the Netherlands) and X-ray diffraction (XRD) (D76181 Karlsruhe, Germany). To identify the surface functional groups, Fourier transform infrared (FT-IR) analysis was performed with a Spectrum One spectrometer (Nicolet Magna-IR 750, USA) from 400 to 4,000 cm\(^{-1}\) by dried KBr pellets. Zeta potentials of NZ before and after TC and Cu adsorption were determined at different pH levels using a Zeta potential meter (Malvern, UK).

The concentrations of TC and Cu(II) in the aqueous solution were determined by reversed-phase high performance liquid chromatography and inductively coupled plasma mass spectrometry, respectively (supplementary information).

**Statistical analysis**

The statistical differences between samples were analyzed using SPSS Statistics ver. 21.0 software (IBM Corp., Armonk, NY, USA) and \( p < 0.05 \) was considered to be statistically significant. In this study, all the experiments were carried out in triplicate, and data from the triplicates for each treatment (relative standard deviation <5%) were subjected to an analysis of variance.

**RESULTS AND DISCUSSION**

**Characterization of NZ**

The most significant signals in the XRD pattern of NZ (Figure S1(a); Figure S1 is available with the online version of this paper) were at 2\( \theta \) values of 11.18\(^{\circ}\), 13.06\(^{\circ}\), 16.92\(^{\circ}\), 17.36\(^{\circ}\), 19.06\(^{\circ}\), 20.08\(^{\circ}\), 22.42\(^{\circ}\), 22.74\(^{\circ}\), 26.62\(^{\circ}\), 28.14\(^{\circ}\), 30.06\(^{\circ}\), and 32.02\(^{\circ}\). Identification of the phase showed that NZ was crystalline, and the main constituents were Al\(_2\)SiO\(_5\), Ca AlO\(_4\), and CaAl\(_2\)Si\(_2\)O\(_8\), indicating that NZ was mostly composed of metal-Si oxide. The SEM images (Figure S1(b)) of NZ showed that some crystals are apparently fused together to form agglomerate particles and are uniform in size. Further, the EDX results showed that NZ contained 46.66% O, 34.46% Si, 8.27% Ca and 5.56% Al in weight, suggesting that the primary components of the adsorbent were SiO\(_2\) and metal-Si oxide.

**Adsorption performance**

**Effect of Cu(II) concentration**

The amount of TC adsorbed on NZ increased as Cu\(^{2+}\) concentration increased from 0 to 0.01 mmol/L (Figure 1). The optimum adsorption capacity of NZ was approximately 0.5 mg/g of TC, and 99% of the total TC was removed. This indicated that the addition of Cu(II) promoted TC adsorption on NZ, which was also found previously using other adsorbents (Huang et al. 2017; Qin et al. 2018). However, when Cu(II) concentration was further increased to 0.1 mmol/L, the adsorbed amount decreased, indicating that excess Cu(II) could reduce the amount of TC adsorbed on NZ.
Effect of initial pH

As the initial pH increased, the amount of TC adsorbed gradually decreased (Figure 2(a)) in the absence of Cu\textsuperscript{2+}. A similar phenomenon was found in other studies (Hsu et al. 2018; Tabrizian et al. 2019), attributed to the different species of TC at different levels of pH. TC is an amphoteric molecule with multiple ionizable functional groups (Figure S2, available online). The predominance of the TC species is H\textsubscript{3}TC\textsuperscript{+} at pH < 3.3, H\textsubscript{2}TC\textsuperscript{0} at 3.3 < pH < 7.7, HTC\textsuperscript{−} at 7.7 < pH < 9.7, and TC\textsuperscript{2−} at pH > 9.7 (Qin et al. 2018). TC became more negatively charged as pH increased. Because the surface of NZ was mainly negatively charged (Figure 2(b)), the repulsive force between TC and NZ increased with increasing pH, resulting in decreased adsorption. Zeta potential of NZ increased after adsorption of TC when pH was lower than 4 and decreased slightly when pH was higher than 4, suggesting that TC adsorption by NZ may involve charge neutralization at lower pH.

However, with Cu\textsuperscript{2+} present, the influence of pH on the adsorption of TC by NZ was different. High Cu(II) concentration resulted in low adsorption at low pH (2.0–7.0) and high adsorption at high pH (7.0–10.0) (Figure 2(a)). The first effect was due to the fact that TC species carry more positive charges under higher Cu(II) concentrations, and exhibit higher electrostatic interactions with TCH\textsuperscript{−} and TC\textsuperscript{2−} (Zhang et al. 2011). The second effect may be because, under lower pH (2.0–7.0), excessive Cu(II) may compete with TC for adsorption sites on the surface of NZ (Zhou et al. 2017). At higher pH (7.0–10.0), the higher amount of adsorption may be attributed to the precipitation of Cu(II) owing to high concentration of OH\textsuperscript{−}.

Adsorption mechanisms

Kinetics

Analysis of adsorption kinetics and fitting of kinetic models can be used to determine the adsorption type and mechanism. The pseudo-second-order kinetics described the adsorption process better (R\textsuperscript{2} > 0.99) compared to the first-order and second-order kinetics (Table 1). As the pseudo-second-order model is based on the concept that the rate-limiting step may involve valence forces through sharing or exchange of electrons between adsorbent and adsorbate (Chang et al. 2018), the adsorption of TC by NZ may be chemisorption that probably occurs via surface complexation reactions at specific adsorption sites. The increase of the added Cu\textsuperscript{2+} concentration did not change the fitting
correlation of the kinetic equation. In addition, as \( \text{Cu}^{2+} \) concentration increased, the kinetic rate constant \( (k_2^0) \) increased gradually, which also indicated that the increase of \( \text{Cu}^{2+} \) concentration helps to accelerate the adsorption process of TC on NZ.

<table>
<thead>
<tr>
<th>Concentration of ( \text{Cu}^{2+} ) (mmol/L)</th>
<th>Pseudo-first order</th>
<th>Second-order</th>
<th>Pseudo-second-order</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Cu}^{2+} ) concentration (mmol/L)</td>
<td>( k_1 )</td>
<td>( \ln q_e )</td>
<td>( R^2 )</td>
</tr>
<tr>
<td>0</td>
<td>1.267</td>
<td>-1.498</td>
<td>0.835</td>
</tr>
<tr>
<td>0.001</td>
<td>1.671</td>
<td>-1.593</td>
<td>0.818</td>
</tr>
<tr>
<td>0.01</td>
<td>1.879</td>
<td>-1.371</td>
<td>0.897</td>
</tr>
<tr>
<td>0.1</td>
<td>2.356</td>
<td>-2.244</td>
<td>0.663</td>
</tr>
</tbody>
</table>

Table 2 | Effect of \( \text{Cu}^{2+} \) concentration on Langmuir and Freundlich adsorption isotherm parameters of TC adsorption on NZ (initial TC concentration = 0–100 mg/L, adsorbent dosage = 40 g/L)

<table>
<thead>
<tr>
<th>Concentration of ( \text{Cu}^{2+} ) (mmol/L)</th>
<th>Langmuir isotherm</th>
<th>Freundlich isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td>( q_e^\infty )</td>
<td>( K_L )</td>
<td>( R^2 )</td>
</tr>
<tr>
<td>0</td>
<td>1.228</td>
<td>0.069</td>
</tr>
<tr>
<td>0.001</td>
<td>1.242</td>
<td>0.118</td>
</tr>
<tr>
<td>0.01</td>
<td>2.003</td>
<td>0.114</td>
</tr>
<tr>
<td>0.1</td>
<td>0.706</td>
<td>0.223</td>
</tr>
</tbody>
</table>

Isotherms

With low level \( \text{Cu}^{2+} \) (0–0.1 mmol/L), the Langmuir adsorption isotherm equation fitted better for the adsorption (Table 2 and Figure 3). However, when the \( \text{Cu}^{2+} \) concentration was 0.001 and 0.01 mmol/L, the Freundlich isotherm equation was more fitting. The Langmuir model is an equation based on the single-layer adsorption theory, while the Freundlich model is an empirical model developed on the basis of the multi-layer adsorption theory (Jang et al. 2018). The results indicated that \( \text{Cu}^{2+} \) may change the nature of isothermal adsorption, thereby changing the adsorption mechanism of TC on NZ. This result was inconsistent with previous studies, which showed that TC adsorption fitted better with one model only (Jang et al. 2018; Zhang et al. 2018). This may be

![Figure 3](https://iwaponline.com/wst/article-pdf/80/1/164/600002/wst080010164.pdf)
explained as follows: (1) the adsorbents differed in these studies; and/or (2) the addition of Cu(II) may change the adsorption mechanism. As the Cu²⁺ increases, the $n$ value also increases gradually, and the value was over 1, indicating that preferential adsorption and the increased concentration of Cu(II) promoted the adsorption of TC by NZ (Ahmed et al. 2017).

Potential competitive adsorption of TCs and Cu(II)

To further evaluate the competitive adsorption behaviors of TC and Cu(II) on NZ, binary adsorption experiments were conducted. Low level of Cu(II) enhanced TC adsorption, whereas the residual TC increased as Cu(II) concentration increased from 0.01 to 1 mmol/L (Figure 4). The residual Cu(II) in the solution decreased as the TC increased from 0 to 20 mg/L. However, as TC further increased, the residual Cu(II) concentration increased, suggesting that Cu(II) adsorption on NZ is suppressed by a high concentration of coexisting TC. Similar observations were reported by Zhou et al. (2017), which may be due to the complexion interaction between TC and Cu only occurring at low concentrations, and competition between the two for an adsorption site existing at high concentrations.

FT-IR analysis of NZ

A preliminary qualitative analysis of the vibration frequency changes of the main functional groups of NZ before and after adsorption was assessed by FT-IR (Figure 5).

The spectrum of pure NZ showed adsorption bands 3,625, 3,489, 1,649, 1,225, 1,082, 805, and 605 cm⁻¹. According to previous studies (Guo et al. 2017; Ali et al. 2018; Wang et al. 2018), these bands can be explained as follows: (i) the bands around 3,625 and 3,489 cm⁻¹ were attributed to the adsorbed molecular water and hydroxyl groups; (ii) the peak at 1,649 cm⁻¹ was ascribed to the stretching vibration of C=O in ketones, lactones, and the carboxyl group; (iii) the band at 1,225 cm⁻¹ may be attributed to O-H groups; (iv) the band around 1,082 cm⁻¹ was attributed to C-O-C or C-OH groups; and (v) the bands around 805 and 605 cm⁻¹ may correspond to the Al-O or Si-O groups, as NZ was affected by aluminum oxide and silicon oxide.

Compared with pure NZ, significant changes in the FT-IR spectrum were found after the contact of TC with NZ. The peaks at 3,625 and 3,489 cm⁻¹ were broader after adsorption of TC, suggesting that the molecular water adsorbed on NZ decreased, or that hydroxyl groups were involved in the adsorption of TC.

Under the coexistence of TC and Cu, there were several changes in the FT-IR spectrum of NZ as follows: (i) the peak at 1,225 cm⁻¹ disappeared after TC and Cu(II) adsorption, suggesting that OH groups and a coordination complex may occur among NZ and the two adsorbates; (ii) the bands at 1,082 and 805 cm⁻¹ shifted to 1,045 and 785 cm⁻¹ after TC and Cu(II) adsorption respectively, indicating that these groups participated in the adsorption reaction; and (iii) the peak at 605 cm⁻¹ disappeared after TC and Cu(II) adsorption. Several types of interactions may occur between TC and Cu atoms: (i) TC can strongly bind to Cu atoms through the NH₂ group (Mondal et al. 2016; Singuru et al. 2018).
and form larger-size aggregates (Mondal et al. 2016), thereby blocking the pores of the zeolite.

NZ showed the best TC adsorption capacity among several commonly used natural materials we have evaluated (Table S2, available online). Additionally, it showed a TC adsorption capacity commensurate with other natural materials such as marine sediment (Fei & Li 2013), but it was much easier to obtain. Although the TC adsorption capacity of NZ was lower than those of other synthetic adsorbents, such as mesoporous carbon (Junyu et al. 2019), Cu(II)-modified hierarchical ZSM-5 (Fan et al. 2019), and CoO/CuFe2O4 (Ifebajo et al. 2018), its cost is much lower than them. This has widened its application prospects for TC removal. Additionally, the diameter of NZ herein is 5–8 mm, indicating that the adsorbed amount can be further enhanced by decreasing the particle size.

Compared with single pollutant, the combined pollution of antibiotics and heavy metals increases the difficulty of their removal. Our study suggests that the Cu/TC ratio may affect the adsorption performance of the adsorbent. Additionally, given the right conditions, one major antibiotic pollutant in our environment can accelerate the removal of another. Therefore, it is important to comprehensively investigate the concentration level of pollutants, not only TC and Cu(II), in the environment and adopt appropriate treatment technologies for pollutants according to their concentration levels.

CONCLUSIONS

In this work, the effect of Cu(II) on TC adsorption by NZ was investigated. The addition of low concentration (<0.01 mmol/L) of Cu(II) enhanced the TC adsorption on NZ, but excess Cu(II) suppressed TC adsorption. Cu(II) did not change the best-fit kinetic model but changed the nature of the adsorption isotherm from Langmuir type to Freundlich type as Cu(II) increased, suggesting a change in the adsorption mechanism of TC on NZ. pH had significant effects on TC removal, and the effect differed with the coexistence of Cu(II). The FT-IR spectrum showed that functional groups on the surface of NZ changed after TC and Cu(II) adsorption, suggesting that complexation reactions occurred on the surface of NZ. The adsorbed amount of both TC and Cu(II) decreased as the concentration of the other pollutant increased, suggesting a competitive adsorption between TC and Cu(II) on NZ. The concentration levels and ratios (such as Cu:TC) should be taken into consideration when adopting appropriate treatment technologies for pollutants.

TC adsorption mechanism on NZ influenced by Cu(II)

The Cu(II)-influenced adsorption mechanisms for TC on NZ were proposed based on the results above. As the results demonstrated in Figures 1 and 2, the addition of a specific amount of Cu²⁺ promoted TC adsorption by NZ. At the optimal Cu(II) concentration (0.01 mmol/L), the mole ratio of Cu to TC was 0.24 (Table S5, available online), which was not the best complexation ratio of Cu and TC. This indicated that the adsorption of TC by NZ was not completely dependent on Cu(II), as NZ could adsorb TC even without Cu(II). Additionally, the increase of the added Cu²⁺ concentration did not change the fitting of the kinetic equation, but the best-fit adsorption isotherm model changed to the Freundlich model when Cu(II) coexisted (Table 2), indicating that the coexistence of Cu(II) changed the adsorption mechanisms, and multi-layer adsorption may be involved in TC adsorption with Cu(II) present.

TC species carry more positive charges with Cu(II), resulting in an increased electrostatic interaction between TC and NZ. Additionally, there were several changes in the FT-IR spectrum of NZ after the adsorption of TC and Cu(II) (NZ + TC + Cu(II)), compared with spectra of NZ and ‘NZ + TC’ (Figure 5). This confirmed the reaction between TC, Cu(II), and the functional groups of NZ. Previous studies showed that the ion exchange of Cu with zeolite replaced the metal site of zeolite (Al and Si) by Cu (Barrer & Townsend 1976; Öhman et al. 2002). The ion-exchanged Cu(II) on NZ can form bonds with TC, following which TC can be adsorbed by NZ. In this case, the Cu acts as a bridge between zeolite and TC for the TC adsorption.

However, excess Cu(II) suppressed TC adsorption (Figures 1 and 2). This could be explained by two factors. The first factor was the competitive adsorption between TC and Cu(II). High concentration of Cu(II) decreased TC adsorption, while the addition of a high concentration of TC also led to decreased Cu(II) removal (Figure 4), indicating that the two adsorbates competed for the adsorption sites of NZ. Second, Cu atoms may enter the pores of NZ and form larger-size aggregates (Mondal et al. 2016), thereby blocking the pores of the zeolite.

(ii) the aromatic ring of TC can form a bond with the Cu site via van der Waals interactions (Mondal et al. 2016; Quang Thang et al. 2017); (iii) the binding energy of the OH group with the Cu site has been reported to be ~70 kJ/mol (Amaniampong et al. 2018b; Quang Thang et al. 2018); (iv) the C=O group could also form a weak bond with the Cu site (Amaniampong et al. 2018a). The results of FT-IR analysis confirmed that NZ reacted with TC and Cu(II) during the adsorption.
ACKNOWLEDGEMENTS

This work was supported by the National Natural Science Foundation of China (grant number 51708034), and Special Project for Science and Technology Innovation of the Beijing Academy of Agriculture and Forestry Sciences (grant number KJCX20180417 and KJCX20180708).

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