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Decontamination of lead and tetracycline from aqueous solution by a promising carbonaceous nanocomposite: Interaction and mechanisms insight



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ABSTRACT

Innovative carbonaceous nano-chlorapatites (CNClAPs) which originated from the pyrolyzation of the mixture of bamboo residues and chlorapatites varying from 400 °C to 600 °C were used to investigate the decontamination efficacy of lead (Pb²⁺) and tetracycline (TC) from wastewater. Rising pyrolytic temperature can highly improve the decontamination efficacy, of which CNClAP600 exhibited the most remarkable effects for Pb²⁺ and TC decontamination (90.37% for Pb²⁺ and 86.58% for TC at pH = 7). The kinetic, isotherm and characterization analysis demonstrated that the inner mechanisms for the decontamination of Pb²⁺ and TC involved precipitation, electrostatic interaction, hydrogen bonding, π - π interaction and pore filling. Experiment indicated that the enhancement and competitive adsorption resulted from the interaction between Pb²⁺ and TC could facilitate their joint decontamination under low concentrations. This research shed light on the management of coexisting heavy metals and organic matters contamination in wastewater by CNClAPs under different temperatures.

1. Introduction

Lead (Pb) has been considered as one of the most threatening and nocuous heavy metals in the environment (Huang et al., 2017a; Xue et al., 2017). It might pose a significant threat to human health such as

infant hemolytic disease, oligos and bone damage, cancer and even death when it was ingested through the food chain (Gong et al., 2017; Huang et al., 2018b). Besides, China is a major country in the production, use and sale of antibiotics in the world (Hu et al., 2018; Huang et al., 2017b; Huang et al., 2017c). Tetracycline (TC) is one of the most

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common antibiotics in the agriculture and livestock industry (Huang et al., 2018c; Wang et al., 2019). However, it has been reported that not all of the TC can be absorbed by animals after they come into the environment (Huang et al., 2019a; Wang et al., 2016a). Incomplete metabolism of animals can cause approximately 30%–90% of TC to discharge into aquatic environments in the form of parent compounds which might induce multi-resistant genes in microorganisms and eventually cause the existing medicines to fail to function, consequently posing a threat to human health (Wang et al., 2018a). Therefore, finding effective methods to decontaminate heavy metals and organics from aquatic environment is impending (Huang et al., 2016a; Huang et al., 2016c).

Adsorption is considered as an efficient, low-cost and environmentally friendly method for the removal of heavy metals and organic matters (Wang et al., 2014; Wang et al., 2016b). Biochar, which is obtained from various wastes, sewage sludge and some other low-cost raw materials, has been used as an environmentally friendly adsorbent for the decontamination of environmental contaminants over the years (Ahmed et al., 2016; Gong et al., 2018). Previous research revealed that biochar presented higher sorption capacity than commercial active carbon for Pb²⁺ and some other heavy metals (Kołodyńska et al., 2017). And Aghababaei et al., (2017) have used different types of biochar to simultaneously remove cadmium (Cd) and TC from aqueous solutions which showed excellent removal efficacy.

However, the pristine biochar (PBC) cannot satisfy progressively increasing contaminants in aqueous solutions, especially high concentrations of contaminative water (Huang et al., 2017d). Hence, seeking more effective biochar technology to control environmental contamination is really great of significance (Huang et al., 2019c). Carbonaceous nanocomposites which possessed better physicochemical properties, simple preparation and prominent decontamination efficacy for environment contaminants have been concerned recent years (Huang et al., 2018a). It exhibited a win-win benefit for both the development of biochar technologies and water contamination control (Wang et al., 2018d). For example, graphene supported by biochar was applied to decontaminate organic and inorganic contaminants which obtained a remarkable effect (Tang et al., 2015). A novel carbonaceous nanocomposite which combined biochar with multi-walled carbon nanotube was fabricated to sorb sulfamethazine from aqueous solution (Zhang et al., 2016).

Chlorapatites (ClAP) have well aptitudes for Pb remediation since the phosphates of Pb [Pb₅(PO₄)₃Cl, Ksp 10^{-84.4}] were much less soluble than other Pb compounds (Zeng et al., 2017). Hence, CIAP could cooperate well with Pb and convert it from unstable fraction to stable fraction. Previous research has successfully synthesized ClAP materials to remediate Pb-contaminated sediments, which showed remarkable remediation efficacy (Wan et al., 2018). Generally, in the real aquatic environment, not just a single contaminant exists, but a variety of contaminants generally coexist (Guo et al., 2018). And due to the complexity of the water environment, studies have not determined whether chlorapatite can remove heavy metals and other contaminants in the water environment. Hence, considering the properties of biochar and chlorapatite, this research has fabricated three novel carbonaceous nano-chlorapatites (CNClAPs) which combined biochar with ClAP under the pyrolysis temperature of 400 °C, 500 °C and 600 °C. Then they were applied for the decontamination of Pb²⁺ and TC from wastewater and brought deep insight into the inner mechanisms involving chemisorption of Pb²⁺ and TC decontamination. The aims of this work were to: (1) fabricate CNClAPs under different temperatures; (2) investigate the efficiencies and mechanisms of CNClAPs to decontaminate Pb²⁺ and TC from aqueous solutions; (3) study the interactions between Pb^{2+} and TC; (4) explore the real water application.

2. Materials and methods

2.1. Materials and chemicals

Tetracycline (TC: purity > 98.5%) and lead nitrate $(Pb(NO_3)_2, purity > 99\%)$ were acquired from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China) and Xilong chemical co. Ltd (Guangdong, China), respectively. The bamboo residue was obtained from local farmers in Changsha. Uultra-pure grade water (18.25 M\Omega.cm) was used for all experiments.

2.2. Preparation of materials

PBC was slowly pyrolyzed by bamboo residue in tube furnace under the protection of nitrogen at 600 °C for 2 h and the heating rate of pyrolysis was at 7 °C min⁻¹ (Huang et al., 2016b).

Preparation of CNCIAPs: Firstly, the preparation of CIAP was on the basis of previous research (Wan et al., 2016). And then the prepared chlorapatite was stirred continuously with the addition of a given mass of bamboo residue (dried and kibbling). After 48 h, these suspensions were centrifuged and dried at 60 °C for 12 h. Then the dry mixture was put into tube furnace to pyrolyze at different temperatures (400–600 °C). The pyrolysis process was totally the same as PBC. Finally, the CNCIAPs were obtained and stored in the dryer for later use.

2.3. Batch experiment and characterization methods

The batch experiments were displayed in Supplementary Materials. The surface morphology of materials was examined by Scanning electron microscopy (SEM, JSM-6700F). Brunauer-Emmett-Teller surface analyzer (BET, NOVA 1000 e, Quantachrome Instruments) was used to measure the specific surface area and pore values of materials. X-ray photoelectron spectroscopy (XPS, *K-Alpha* 1063, UK) was utilized to test the materials elements binding energies. X-ray diffractometer (XRD-6100, SHIMADZU) was used to identify the crystalline constituents of materials. To investigate the functional groups on the surface of materials, fourier transform infrared spectrum (FTIR) measurements were conducted in the range of 4000–400 cm⁻¹ with KBr pellet method by Nicolet 5700 Spectrometer, USA. A zeta potential meter (Zetasizer Nano-ZS90, Malvern) was used to analyze the zeta potentials of materials in water solutions.

3. Results and discussions

3.1. Effect of pH on Pb^{2+} and TC decontamination

pH can alter both surface properties of contaminants and materials in aqueous solution, including the functional groups of the materials, the ionization degree of contaminants and so on (Aghababaei et al., 2017). Fig. 1 showed the influence of the initial solution pH (from 2.0 to 7.0) on the decontamination efficacy of Pb²⁺ and TC by PBC, ClAP and CNCIAPs. As displayed in Fig. 1, the decontamination efficacy of CNClAPs were obviously higher than PBC and ClAP, which stated that the decontamination efficacy of Pb²⁺ and TC were both well promoted by the introduction of chlorapatites onto biochar. Moreover, the decontamination efficacy of Pb²⁺ and TC obviously increased with the rising temperature on CNClAPs. CNClAP600 exhibited the best decontamination efficacy for Pb2+ and TC, indicating the pyrolytic temperature can highly influence the properties of CNClAPs which also benefited for Pb²⁺ and TC decontamination. For Pb²⁺, the adsorption capacities were gradually increased with the increasing pH. As reported by previous research, the solution pH can highly influence the behavior of the oxygen-containing groups which existed on the surface of biochar materials (i.e., carboxylate and hydroxyl) (Wang et al., 2018c). The results of zeta potential indicated that the surface of materials displayed in positively charged form at low pH, which might be since most of



Fig. 1. The effects of different pH values ranging from 2.0 to 7.0 on Pb^{2+} (a) and TC (b) decontamination in aqueous solution. The error bars represent the standard deviation of the means (n = 3).

these oxygen-containing groups on materials surface were protonated (Supplementary Materials). The zero potential point (pH_{zpc}) of five materials were a bit different, but all were around 3.40. As the pH <pH_{zpc}, the surface of PBC, ClAP and CNClAPs carried positive charge and the electrostatic repulsion between the positive charge and Pb2+ might result in poorer decontamination efficacy of Pb²⁺. Besides, there are plenty of H^+ and H_3O^+ in the aqueous solution which might compete with Pb²⁺ for adsorption sites on materials, finally limiting the decontamination process. However, the positive charge of the materials and H⁺, H₃O⁺ gradually declined which lead the competitive effect weakened and decontamination efficacy increased with the pH increasing (Fig. 1a). As the pH $> pH_{zpc}$, the negative charge appeared on the surface of materials. In this moment, the electrostatic attraction between the negative charge on the surface of materials and Pb²⁺ would dominate the decontamination process, resulting the highest decontamination efficacy in pH = 7 for Pb^{2+} . And the stabilization mechanism of Pb²⁺ by ClAP have been proposed by previous research and displayed in (Eqs. (1)-(3)) (Wan et al., 2018). Hence, the Pb²⁺ can be easily captured by the surface of materials at higher pH due to electrostatic attraction which promote the formation of Pb₅(PO₄)₃Cl.

$$\operatorname{Ca}_{5}(\operatorname{PO}_{4})_{3}\operatorname{Cl} + 6\operatorname{H}^{+} \xrightarrow{\operatorname{dissolution}} 5\operatorname{Ca}^{2+} + 3\operatorname{H}_{2}\operatorname{PO}_{4}^{-} + \operatorname{Cl}^{-}$$
(1)

$$5Pb^{2+} + 3H_2PO_4^- + Cl^- \xrightarrow{\text{precipitation}} Pb_5(PO_4)_3Cl\downarrow$$
 (2)

$$Ca_{5}(PO_{4})_{3}Cl + xPb^{2} + \xrightarrow{substitution} (Ca_{5-x}Pb_{x})(PO_{4})_{3}Cl + xCa^{2+}$$
(3)

Apart from the charge on the surface of materials can be changed with different pH values, the organic compound can also change the chemical speciation by protonation and deprotonation transition of functional groups at different pH values (Zeng et al., 2019). TC exists multiple ionizable functional groups which can form a number of species at different pH levels because it is an amphoteric molecule and the TC species are TC^{3+} at pH < 3.3, TCH_2^0 at 3.3 < pH < 7.7, TCH^- at 7.7 < pH < 9.7, and TC^{2-} at pH > 9.7 (Zhou et al., 2017). As displayed in Fig. 1b, the decontamination efficacy of TC at the pH values ranging from 2.0 to 4.0 were gradually increased and then slightly declined after pH > 4. The electrostatic repulsion between TCH³⁺ and the positive charge on the surface of materials dominated the decontamination process at low pH (pH $< pH_{zpc}$). Moreover, the decontamination efficacy of TC was increased with the pH increasing between 2.0 and 4.0 which might be due to the weakening of electrostatic repulsion. When the pH of solution was between 4.0 and 7.0, the surface of materials carried negative charge and the main existence form of TC in aqueous solution is TCH₂⁰. There are almost no net electrical charges of TC in aqueous solution, which resulted little electrostatic interactions between TC and materials. At this time, the interactions of hydrogenbonding, π - π electron donor-acceptor interactions and oxygen-containing functional groups may play an important role without resistance (electrostatic repulsion), leading to well decontamination efficacy of PBC, ClAP and CNClAPs at pH values ranging of 4.0–7.0.

Consequently, the decontamination process of Pb^{2+} and TC were both pH-dependent procedures. The decontamination efficacy of TC increased with the pH values from 2.0 to 4.0 and slightly declined from 4.0 to 7.0. As for Pb^{2+} , the decontamination efficacy was promoted with the increasing pH from 2.0 to 7.0 and reached highest adsorption capacities at pH = 7. As shown in Fig. 1, although the highest adsorption capacities of TC were at pH = 4, that of Pb^{2+} were low. The decontamination efficacy of Pb^{2+} and TC were both relatively well at pH = 7.0. Hence, this pH value was chosen for the further decontamination experiments.

3.2. Effect of equilibration time and kinetics models

In Fig. 2, it was found that the decontamination efficacy of Pb^{2+} and TC were both time-dependent procedures. The adsorption capacities of Pb²⁺ and TC were increased with the increasing contact time, which could be probably assigned to the existence of abundant active sites and attractive electrostatic interaction on the surface of PBC, CIAP and CNClAPs. The adsorption capacities increased rapidly in the first 3 h and then slowed down until the adsorption equilibrium. CNClAP600 exhibited the best performance for the decontamination of $\mbox{Pb}^{2\,+}$ and TC and the adsorption capacities of $\ensuremath{Pb^{2+}}$ and TC can reach to $180.74\,mg\,g^{-1}$ and $34.63\,mg\,g^{-1},$ which accounted for 90.37% and 86.58% of its total adsorption capacities in the first 3 h at pH = 7, respectively. It might be since that the chlorapatites can easily combine with Pb²⁺ and formed Pb₅(PO₄)₃Cl, resulting in the higher decontamination efficacy of Pb²⁺ than TC at 600 °C. But for TC, the adsorption capacities were more influenced by the surface structures of materials which were not dominated by precipitation like Pb²⁺. Hence, higher temperature can highly change the surface structures of CNClAPs (i.e., surface area and functional groups) which can improve the adsorption performance of TC. Fig. 2 revealed that the adsorption capacities of Pb²⁺ and TC were both increased with the increasing contact time, but the adsorbed rate gradually declined until the adsorption capacities had no significant variation after adsorption equilibrium. In order to make the full reaction between materials and contaminants, 24 h was chosen as the contact time for further experiment.

In order to further investigate the mechanisms of Pb^{2+} and TC by PBC, ClAP and CNClAPs, kinetic models (the pseudo-first-order and pseudo-second-order) were adopted. The expression of these two models can be generalized in Eqs. (4) and (5) (Wang et al., 2018c):



Fig. 2. The effects of contact time and their sorption kinetics using PBC, ClAP and CNClAPs on the decontamination of Pb^{2+} and TC: (a) the pseudo-first-order plots of Pb^{2+} ; (b) the pseudo-first-order plots of TC, (c) the pseudo-second-order plots of Pb^{2+} ; (d) the pseudo-second-order plots of TC.

$$\frac{\mathrm{d}Q_{\mathrm{t}}}{\mathrm{d}_{\mathrm{t}}} = \mathrm{k}_{\mathrm{i}}(\mathrm{Q}_{\mathrm{e}} - \mathrm{Q}_{\mathrm{t}}) \tag{4}$$

$$\frac{\mathrm{d}Q_{\mathrm{t}}}{\mathrm{d}_{\mathrm{t}}} = k_2 (Q_{\mathrm{e}} - Q_{\mathrm{t}})^2 \tag{5}$$

where $Q_t (mg g^{-1})$ is the adsorption capacities of Pb^{2+} and TC at time t and $Q_e (mg g^{-1})$ is the adsorption capacities of equilibrium; $K_1 (min^{-1})$ and $K_2 (g mg^{-1} min^{-1})$ are the adsorption rate constants of pseudofirst-order and pseudo-second-order models. The pseudo-first-order models of Pb^{2+} and TC decontamination were displayed in Fig. 2a and b, while the pseudo-second-order models were shown in Fig. 2c and d, and the relative kinetic parameters were summarized in Supplementary Materials. As presented in Fig. 2, the pseudo-second-order model was more suitable for the adsorption behavior compared with the pseudofirst-order models due to the higher values of correlation coefficient (R^2). The experimental data ($Q_{e_{P}exp}$) are more approximate the calculated values ($Q_{e_{P}cal}$) to pseudo second-order model, which also indicated that the adsorption behavior of Pb^{2+} and TC fitted better to the pseudo second-order model and was highly influenced by chemical mechanism (Supplementary Materials).

3.3. Effect of initial concentration and isotherms models

Adsorption isotherm model is a vitally important model in heavy metals and organic contaminants decontamination from aqueous solution. It can display the distribution of solute molecules in aqueous solution and optimizes the use of adsorbents because it describes how adsorbates interact with adsorbents (Tan et al., 2015). Fig. 3 exhibited

the enhanced adsorption capacities (Q_e) of Pb^{2+} and TC after equilibrium with the increasing initial concentration of Pb^{2+} and TC (C_e) in the range of $10-300 \text{ mg L}^{-1}$. The maximal adsorption capacity of CNClAP600, CNClAP500, CNClAP400, ClAP and PBC for Pb²⁺ were 215.86, 142.02, 135.48, 78.12 and 62.28 mg kg⁻¹, while 128.69, 121.34, 114.14, 105.51 and 58.63 mg kg⁻¹ for TC, respectively. It was observed that the increasing of adsorption capacities of Pb²⁺ and TC were both not conspicuous after 100 mg L^{-1} . This phenomenon can be ascribed to the limited adsorption sites on per unit mass of materials when it reached the maximal adsorption capacity. However, when the initial concentration of Pb^{2+} and TC were 100 mg L⁻¹ and 20 mg L⁻¹, CNClAP600 exhibited the most remarkable effects for Pb²⁺ and TC decontamination and the maximum adsorption rates of $\ensuremath{\mathsf{Pb}^{2+}}$ and TC were 90.37% and 86.58%. The adsorption rates sharply declined as the initial concentration of Pb^{2+} and TC exceeded 100 mg L^{-1} and 20 mg L^{-1} . Hence, 100 mg L^{-1} and 20 mg L^{-1} were chosen as the optimal initial concentrations of Pb^{2+} and TC in this research.

Hence, in order to further explore the adsorption mechanism of Pb^{2+} and TC on the surface of PBC, CIAP and CNCIAPs, two isotherm models of Langmuir and Freundlich model were used to fit the adsorption behavior of Pb^{2+} and TC. The expression of these two models can be generalized in Eqs. (6) and (7):

$$Q_e = \frac{KQC_e}{1 + K_LC_e}$$
(6)

$$Q_e = K_F C e^n \tag{7}$$

where K_L and K_F are considered as related constants for affinity between the adsorbent and binding site; Q_e is the saturated extent of adsorption



Fig. 3. The effects of initial concentration of Pb^{2+} and TC and sorption isotherms using PBC, ClAP and CNClAPs for the decontamination of Pb^{2+} and TC: (a) the Langmuir model simulation of Pb^{2+} ; (b) the Langmuir model simulation of TC, (c) the Freundlich model simulation of Pb^{2+} ; (d) the Freundlich model simulation of TC.

(mg g⁻¹); C_e is the initial solution concentration of Pb²⁺ and TC (mg L⁻¹); n represents the linear constant of Freundlich models, smaller values of n generally indicate better adsorption performance of materials.

Langmuir model assumes that it is a monolayer molecular adsorption on specific uniform sites which emphasizes no interactions between adsorbate molecules (Huang et al., 2019b). Fig. 3a and b showed the Langmuir models of Pb²⁺ and TC decontamination. The Langmuir models fitted the isotherm data well with prominent correlation coefficients ($R^2 > 0.96$), indicating that the adsorption behavior Pb²⁺ and TC by PBC, CIAP and CNCIAPs possibly could be regarded as monolayer molecular adsorption and was highly influenced by functions of chemical mechanism. What was noteworthy was that the equilibrium stability constant K₁ of Langmuir model was found to be between 0 and 1, which also indicated that the adsorption of Pb²⁺ and TC on the surface of PBC and CNCIAPs probably was a homogeneous monolayer adsorption process and the adsorption process is favorable (Table 1).

Freundlich model is a hypothesis of multilayer heterogeneous surface adsorption (Zhou et al., 2013). As displayed in Fig. 3c and d, the experimental data of TC fitted better with Freundlich model than Pb²⁺. The correlation coefficients (R^2) of TC were all greater than 0.948, indicating that the TC adsorption by PBC and CNCIAPs also involved the physical interaction. However, the correlation coefficients (R^2) of Pb²⁺ were clearly lower than TC and some even under 0.9, which suggested that the chemical mechanism was primarily responsible for Pb²⁺ decontamination (Eqs. (1)–(3)). The K_F values represented the adsorption capacity and it was also in accordance with the decontamination efficacy: CNClAP600 > CNClAP500 > CNClAP400 > ClAP > PBC (Table 1). And it can also be observed that the heterogeneity factors 1/n (which was an essential parameter for the bond distribution description) were all less than 1, indicating that the PBC and CNClAPs, especially CNClAP600 was facile and favorable for the decontamination of Pb²⁺ and TC.

In general, the decontamination of Pb and TC from aqueous solution was primarily controlled by chemical mechanism, but the physical mechanism could also influence the decontamination process and the influence for TC was stronger than Pb^{2+} .

3.4. The interaction between Pb^{2+} and TC

Actual aquatic environment usually existed multiple contaminants at the same time. When two or more than two contaminants appeared in the water environment, the interaction between contaminants was not neglected. This research simulated Pb^{2+} and TC coexistence in aqueous solutions for the first time in this study. Although Pb^{2+} and TC adsorption seem to exist different adsorption mechanisms onto CNCIAPs, but these two contaminants all need adsorption sites on the surface of CNCIAPs. Hence, the investigation of competitive adsorption between Pb^{2+} and TC is necessary. Fig. 4a displayed the influences of various concentrations of TC (0–200 mg L⁻¹) on Pb²⁺ adsorption under the invariable concentration of Pb^{2+} (100 mg L⁻¹). Compared with the single Pb^{2+} sorption system with no TC addition in Fig. 2, it can be seen that the presence of low concentration of TC (2 mg L⁻¹) could highly facilitate the Pb^{2+} adsorption. The adsorbing capacities of PBC, CIAP,

Table 1

| The isotherm models parameters of Langmuir, Freundlich mo | els for the decontamination of F | 'b ²⁺ and TC on PBC ClAP | , and CNClAPs. |
|---|----------------------------------|-------------------------------------|----------------|
|---|----------------------------------|-------------------------------------|----------------|

| Materials | | Langmuir models | | Freundlich mo | Freundlich models | | |
|-----------|----|----------------------|------------------|----------------|-------------------|------------------------------|----------------|
| | | $Q_{max}(mg g^{-1})$ | $K_L(L mg^{-1})$ | \mathbb{R}^2 | 1/n | $K_{\rm F}({\rm L~mg^{-1}})$ | \mathbb{R}^2 |
| РВС | Рb | 81.02 | 0.0128 | 0.9705 | 0.4843 | 4.31 | 0.9166 |
| | TC | 58.63 | 0.0023 | 0.9977 | 0.5281 | 1.62 | 0.9885 |
| ClAP | РЬ | 99.51 | 0.0147 | 0.9601 | 0.4693 | 5.95 | 0.8877 |
| | TC | 105.51 | 0.0024 | 0.9602 | 0.7419 | 1.99 | 0.9799 |
| CNClAP400 | РЬ | 171.05 | 0.0145 | 0.9746 | 0.4785 | 9.72 | 0.9221 |
| | TC | 114.14 | 0.0063 | 0.9759 | 0.6389 | 3.81 | 0.9757 |
| CNClAP500 | Pb | 174.72 | 0.0199 | 0.9781 | 0.4410 | 11.91 | 0.9090 |
| | TC | 121.31 | 0.0064 | 0.9705 | 0.6355 | 4.11 | 0.9926 |
| CNCIAP600 | Pb | 292.87 | 0.0114 | 0.9766 | 0.5275 | 13.08 | 0.9385 |
| | TC | 128.69 | 0.0107 | 0.9932 | 0.5826 | 6.22 | 0.9721 |

CNClAP400, CNClAP500 and CNClAP600 were 128.53, 171.80, 185.18, 193.02 and $198.32 \text{ mg kg}^{-1}$, respectively, which were much higher than that with no TC addition varying as 50.53, 69.94, 108.80, 120.87 and $181.96 \text{ mg kg}^{-1}$, respectively. Expect for CNClAP600, the decontamination efficacy of Pb2+ with PBC, ClAP, CNClAP400 and CNClAP500 were all not very remarkable without TC addition, but they were all promoted after the addition of varying concentration of TC (from 2 to 100 mg L^{-1}). The promotion might be ascribed to the complexation of PBC-Pb²⁺-TC⁰ or CNClAP-Pb²⁺-TC⁰ complex (Zhou et al., 2017). However, the promotion gradually weakened with the increase of TC, which may be due to the increasing competitive adsorption between Pb^{2+} and TC molecules (Fig. 4a). In addition, the CNClAP600 exhibited remarkable decontamination efficacy for Pb²⁺ without TC addition which was over 90%. After the low addition of TC, i.e., 2 mg L^{-1} , it can promote the Pb²⁺ adsorption (from 90.37% to 99.16%). But when more TC were added, it restrained the Pb^{2+} adsorption which might be attributed to the fact that more TC molecules may compete with Pb²⁺, resulting in a decrease in the adsorption capacity of Pb²⁺ onto CNClAP600.

Furthermore, under a fixed initial concentration of TC (20 mg L^{-1}), the impacts of coexisting Pb²⁺ of varying concentrations on TC decontamination were also investigated. As shown in Fig. 4b, it can be found that the adsorption amounts of TC rapidly increased with the initial concentration of Pb²⁺ increasing from 0 to 10 mg L^{-1} . But the adsorption amounts of TC rapidly decreased when Pb²⁺ improved to 20 mg L^{-1} and then gradually leveled off after 20 mg L^{-1} . The strongest inhibiting effect of TC decontamination was 20 mg L^{-1} of Pb²⁺ while the strongest promotion of TC decontamination was in 10 mg L^{-1} of

 Pb^{2+} . The synergetic adsorption dominated the decontamination process of TC under low concentrations of Pb^{2+} coexisting (below 10 mg L^{-1}). The competitive adsorption would gradually replace the promotion impact to take the dominant position for TC decontamination with more addition of Pb^{2+} , resulting in the sorption amounts of TC decreased. And the competitive adsorption was also strongest when the concentration of Pb^{2+} was closer to that of TC.

Consequently, the competitive adsorption between Pb2+ and TC was firstly discussed in research. This parameter is a key issue because not just a single contaminant exists, but multiple contaminants exist concurrently in the environment. It can be observed that significant facilitation was appeared at relatively low concentrations of TC and high concentrations of Pb^{2+} , while the competition was much more strengthen with the increasing concentrations of TC in the fixed primary solute of Pb²⁺. However, when the fixed primary solute was TC, low concentrations of Pb^{2+} can also facilitate the decontamination of TC, but the facilitation was relatively poorer than TC for Pb^{2+} . It is well known that the concentrations of TC usually were with a small quantity in contaminative water. But the heavy metals, especially Pb²⁺, were widespread and numerous due to its non-degradability and cumulativity. Hence, the competitive adsorption results of this research can provide a prospective method for the practical applications of coexisting heavy metals and organic matters contamination in environment.

3.5. Feasible decontamination mechanisms for Pb^{2+} and TC by CNClAPs

Pyrolysis is generally spilt into slow and fast pyrolysis depending on the heating rates. In this research, the bamboo residues and



Fig. 4. The interaction behavior of Pb^{2+} and TC: (a) the influences of various concentrations of TC (0–200 mg L⁻¹) on Pb^{2+} adsorption under the invariable concentration of Pb^{2+} (100 mg L⁻¹); (b) the influences of various concentrations of Pb^{2+} (0–200 mg L⁻¹) on TC adsorption under the invariable concentration of TC (20 mg L⁻¹).

chlorapatites have been co-pyrolyzed under different temperatures by slow pyrolysis. It is mainly since that a high liquid yield (bio-oil) is produced by fast pyrolysis whereas slow pyrolysis obtained solid char as the main product (Mohan et al., 2006). Lower heating rates might allow the chlorapatites have enough time to be better dispersed and eluviated on the surface of the biochar, resulting in a rough or irregular surface structure. Based on the above analysis, the multiple mechanisms and various interactions of CNClAPs for Pb2+ and TC have been speculated. The surface morphologies of PBC, ClAP and CNClAPs were measured by SEM (Supplementary Materials). The SEM image of PBC presented the smooth surface morphology and tubular structures accompanying with some irregular pore structures, while the CLAP displayed a white and clustered structure. The smooth surface morphologies were converted into coarse surface structure covered with a mass of serried white particles on CNClAPs. The white particles on the surface of biochar became more and more dispersed with the increasing temperature which can be observed at the red mark on the image of SEM from CNClAP400 to CNClAP600. It was in accordance with the BET surface area that the specific surface area and pore volumes of CNClAPs were also increasingly improved with the temperature rising from 400 °C to 600 °C (Table 2). Generally, larger specific surface area and pore volumes usually exists abundant adsorption sites and were more beneficial for pore-filling, which could lead to better adsorption capacity.

The white particles in SEM images could be considered as chlorapatites owing to the appearance of P, Cl and Ca peaks in the XPS spectrum of CNClAPs which were determined as the composition of chlorapatites (Supplementary Materials). And the proportion of O element increased significantly after the introduction of the chlorapatite, indicating that more O-containing functional groups appeared due to the introduction of chlorapatite than PBC. The spectra of C 1s peaks were 284.80 eV (C-C), 285.90 eV (C-O) and 287.30 eV (C=O) usually were attached to aliphatic/aromatic carbon and some O-containing moieties (Zhang et al., 2016). From the spectra of O 1s peaks, the peaks at about 531.20, 531.60, 532.90 and 533.50 eV corresponded to CaCO₃, P=O-, C-O and C=O which also suggested that the introduction of chlorapatites brought a mass of O-containing functional groups (Gao et al., 2018). The peak at 347.06 eV could be indexed to a reflection of Ca-P group. Because Fang et al. have reported that parts of Ca-O bandings were converted into Ca-P bandings at 347.06 eV during the reaction of porous calcium silicate hydrate and phosphate which was really in coincidence with the process of chlorapatites fabrication (Fang et al., 2018). The XPS result indicated O-containing functional groups (such as phenolic hydroxyl and carboxylic) play a significant role in Pb²⁺ and TC decontamination (Zhuang et al., 2016).

To give insights into the mechanism of Pb^{2+} and TC decontamination, the XRD and FTIR analysis before and after treatment were demonstrated in Supplementary Materials. As reported by literatures, electrostatic attraction, ion-exchange, physical adsorption, surface precipitation or precipitation might be the possible mechanisms for heavy metals' decontamination from aqueous solution (Ahmad et al., 2014; Wang et al., 2018b). Xu et al., (2013) have reported that mineral components on the surface of biochar, such as CO_3^{2-} and PO_4^{3-} , might serve as additional adsorption sites for heavy metals decontamination. In addition, previous researchers have synthesized a rhamnolipid stabilized nano-chlorapatite to immobilize Pb and Cd contaminated sediment (Wan et al., 2018) which have been confirmed that the formation of Pb₅(PO₄)₃Cl and Cd₅(PO₄)₃Cl might the main dominant mechanisms

| Tal | ble | 2 |
|-----|-----|---|
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| | The | BET | surface | area | of | PBC, | ClAP | and | CNClAPs. |
|--|-----|-----|---------|------|----|------|------|-----|----------|
|--|-----|-----|---------|------|----|------|------|-----|----------|

| Materials | PBC | ClAP | CNClAP400 | CNClAP500 | CNClAP600 |
|--|--------|--------|-----------|-----------|-----------|
| Surface area (m ² g ⁻¹) | 9.4863 | 4.9875 | 5.8111 | 23.6085 | 188.4456 |
| Pore volume (cm ³ g ⁻¹) | 0.0351 | 0.0164 | 0.0251 | 0.0488 | 0.1305 |

for the deactivation of Pb and Cd. Compared with PBC and ClAP, the XRD patterns of ClAP600 appeared the all peaks of PBC and ClAP, which indicated the CNClAPs were successfully fabricated. And the peaks of PBC slightly migrated on the XRD pattern of CNClAP600 which might be that the introduction of ClAP changed the crystal structure of materials. Compared with the CNClAP600 before Pb^{2+} treatment, the peaks of Ca₅(PO₄)₃Cl weakened and some new peaks, Pb₅(PO₄)₃Cl, Pb₃(PO₄)₂ and PbCO₃ appeared in the XRD spectra of CNClAP600 after treatment which also revealed the deactivation process of Pb²⁺ occurred (Supplementary Materials). This process can be can be concluded by Eqs. (1)–(3), further suggesting that surface precipitation was the main mechanisms of Pb^{2+} decontamination (Wan et al., 2018). Besides, the Pb^{2+} decontamination was a pH-dependent procedure (positive effect with the pH values rising), which exhibited that electrostatic interaction was also a significant mechanism (Fig. 2a). Meanwhile, abundant surface functional groups, larger specific surface area and pore values also made a great contribution to the Pb²⁺ decontamination. Hence, as displayed by kinetics and isotherms models, the decontamination procedure of Pb^{2+} was not controlled by a single mechanism but involved integrative effects of several kinds of interactions above.

Generally speaking, the main mechanisms of organic contaminants decontamination were different from heavy metals, including hydrophobic effect, hydrogen bonds, $\pi-\pi$ bonds, electrostatic interaction, pore-filling and so on (Hua et al., 2018; Huang et al., 2017e). From the FTIR analysis in Supplementary Materials, the FTIR spectrum of PBC only existed the obvious peaks of O-H stretching (3450 cm⁻¹) and aromatic C=O, C=C vibration (1592 cm^{-1}) (Chen et al., 2018). The results of FTIR spectra of ClAP, CNClAP400, CNClAP500 and CNClAP600 were similar which suggested that the chlorapatite was successfully introduced onto biochar. Compared with PBC, some new characteristic peaks appeared after the introduction of chlorapatites. such as, 2915 cm⁻¹ for C–H from the stretching vibration of aliphatic (Zhu et al., 2014), 2365 cm^{-1} for cumulated double bonds stretching, 1039 cm⁻¹ for C–O–C, 550 cm⁻¹ for C–H bending vibrations (Wang & Wang, 2018; Zeng et al., 2019). Besides, the peaks of 1430 cm⁻¹ can be assigned to Ca-O vibrations which demonstrated that chlorapatites (Ca₅(PO₄)₃Cl) were primely fabricated and successfully introduced into CNClAP600 (Fang et al., 2018). After adsorption treatment onto TC, the -OH peak at 3450 cm⁻¹ weakened greatly and even disappeared, indicating that H-bonding interactions between the -OH on the surface of CNClAP600 and TC make a great contribution in sorption process. The C=O, C=C peak at 1592 cm^{-1} appeared shifted toward the lower wavenumber side (1536 cm^{-1}) . This change might be owing to the deprotonation of carboxyl, confirming the existence of electrostatic interaction between TC and CNClAPs in adsorption process (Zeng et al., 2019). Moreover, the peaks at 2365 cm^{-1} (cumulated double bonds stretching) and 1592 cm^{-1} (C=O) shifted toward 2357 cm^{-1} and 1536 cm⁻¹ suggested that π - π electron-donor-acceptor interactions may be another important mechanism. Some functional groups of TC molecules (i.e., C=C in benzene rings, C=O, -COOH) may act as π electron acceptors and CNClAPs may act as π-donors. And the Ca-O peak at 1430 cm^{-1} also slightly shifted (1412 cm^{-1}) and weakened which can also be attributed to π - π electron interaction. The FT-IR spectrum of CNClAP600-TC displayed that the peaks approximately at 3500 to 3900 cm⁻¹ were probably originated from the extra functional groups of TC molecule, which can also confirm that CNClAP600 successfully adsorbed TC molecules.

3.6. Real water application

To investigate the practical application of CNClAPs in complex aqueous system, two different water samples, tap water (taken from Changsha Water Supply Company), and river water (derived from Xiangjiang River, China), were used as the medium of Pb^{2+} and TC solution in this research, and the results and discussions were shown in Supplementary Materials.

4. Conclusions

CNClAPs have displayed a considerable decontamination efficacy of Pb^{2+} (90.37%) and TC (86.58%) from wastewater, indicating that the introduction of chlorapatites and pyrolytic temperature highly improved the decontamination efficacy. The competitive adsorption indicated that there existed enhancement and site competition which can facilitate their joint decontamination under low concentrations. Therefore, in consideration of environmental and economic effectiveness of biochar, it is of great significance to investigate more carbonaceous nano-composites to selectively remove multiple contaminants in the actual wastewater in the future.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.biortech.2019.03.086.

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