Nanoconfined Hydrated Zirconium Oxide for Selective Removal of Cu(II)-carboxyl Complexes from High-Salinity Water via Ternary Complex Formation

Xiaolin Zhang, Ping Huang, Siyao Zhu, Ming Hua, and Bing-Cai Pan

Environ. Sci. Technol., Just Accepted Manuscript • DOI: 10.1021/acs.est.9b00745 • Publication Date (Web): 04 Apr 2019

Downloaded from http://pubs.acs.org on April 7, 2019

Just Accepted

“Just Accepted” manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides “Just Accepted” as a service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. “Just Accepted” manuscripts appear in full in PDF format accompanied by an HTML abstract. “Just Accepted” manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are citable by the Digital Object Identifier (DOI®). “Just Accepted” is an optional service offered to authors. Therefore, the “Just Accepted” Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the “Just Accepted” Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these “Just Accepted” manuscripts.
Table of Content
Nanoconfined Hydrated Zirconium Oxide for Selective Removal of 
Cu(II)-carboxyl Complexes from High-Salinity Water via Ternary 
Complex Formation

Xiaolin Zhang,†‡ Ping Huang,† Siyao Zhu,§ Ming Hua,*†‡ Bingcai Pan†‡

† State Key Laboratory of Pollution Control and Resource Reuse, School of the 
Environment, Nanjing University, Nanjing 210023, China
‡ Research Center for Environmental Nanotechnology (ReCENT), Nanjing University, 
Nanjing 210023, China
§ Nanjing Foreign Language School, 30 East Beijng Road, Nanjing 210008, China

* To whom correspondence should be addressed
E-mail: huaming@nju.edu.cn (M.H)
ABSTRACT

Toxic metals are usually present as organic complexes in high-salinity effluents from various industries. The efficient removal of such metal complexes is an imperative but still challenging task due to their stable structure and high mobility. Herein, we propose a new strategy to remove Cu-carboxyl complexes from high-salinity water by using a commercially available nanocomposite HZO-201, i.e., nano-hydrated zirconium oxide (HZO) confined inside anion exchanger D201. In contrast to D201 and a cation exchanger D001 which both adsorb Cu-citrate negligibly, HZO-201 exhibits preferable adsorption toward Cu-citrate (~130 mg Cu/g-Zr) at high salinity (1.5wt% NaCl). Based on STEM-EDS, ATR-FTIR, and XPS analysis, the formation of ternary complex among Cu(II), citrate, and the embedded nano-HZO is evidenced to be responsible for the removal of Cu-citrate. The exhausted HZO-201 can be regenerated with a binary HCl-NaCl solution for repeated use for 5 cycles without capacity loss. Fixed-bed adsorption demonstrates that HZO-201 column is capable of producing ~1150 bed volume (BV) clean water (<0.5 mg Cu/L) from simulated high-salinity wastewater, whereas only ~10 BV and ~60 BV was produced for the D001 and D201 columns, respectively. Furthermore, HZO-201 shows excellent removal of Cu(II) complexes with three other carboxyl ligands (oxalate, tartrate, and succinate).
INTRODUCTION

Because the discharge of wastewater containing toxic metals poses a great threat to ecosystem and public health,\textsuperscript{1, 2} regulations on toxic metal in the discharged wastewater become increasingly stringent. For example, China has set the allowable maximum contaminant level (MCL) of mercury (Hg), nickel (Ni), cadmium (Cd), and copper (Cu) in the discharged industrial effluents as 0.05, 0.1, 0.5, and 0.5 mg/L, respectively.\textsuperscript{3, 4} Chemical precipitation is one of the most widely utilized processes to remove heavy metals from contaminated waters.\textsuperscript{3} Yet, it still remains challenging to reduce heavy metal concentration to sub-ppm level,\textsuperscript{5} raising an urgent need to develop efficient and cost-effective methods for advanced treatment of effluents after chemical precipitation. Previous studies revealed that toxic metals in effluents after precipitation are mainly present in the form of organic complexes, such as carboxyl complex.\textsuperscript{6-8} For instance, considerable amount of Cr (<10 mg/L) still existed in tanning effluent after chemical precipitation, mainly in the form of Cr(III)-carboxyl complexes.\textsuperscript{7} Besides, the addition of precipitants such as NaOH or Ca(OH)\textsubscript{2} increases wastewater salinity remarkably, e.g., >1 wt% salts were detected in electroplating or tanning effluents.\textsuperscript{9, 10} Such high salinity further compromises heavy metal removal efficiency of various methods.\textsuperscript{11, 12}

Removal of toxic metals via adsorption has been extensively studied and widely applied at both laboratory and field scale.\textsuperscript{13-17} A variety of cation exchangers have been commercialized to capture metal ions through electrostatic attraction.\textsuperscript{18} However, heavy metals complexed with organic ligands are often present in the forms of anions or neutral molecules thereby disallowing their adsorption through electrostatic attraction.\textsuperscript{19} Moreover, high salinity remarkably compromises the adsorption of heavy metals onto ion exchangers as the adsorption is dominated by nonspecific interactions.\textsuperscript{20} In the past decades, rapid development of nanotechnology has opened the door for rational design of highly efficient adsorbents for heavy metals.\textsuperscript{3, 21} Nanosized Fe(III), Zr(IV) and Mn(IV) oxides hold a great promise in specifically removing heavy metals due to the abundant hydroxyl groups on their surfaces.\textsuperscript{22-27} With respect to heavy metal-organic complexes, however, the unoccupied orbitals of heavy metals have been
occupied by the electrons in the organic ligands and thus become unavailable to directly
interact with NPs or other adsorbent materials. Although some advanced oxidation
processes (AOPs) have been studied to destroy the organic ligands and thereby to
release the heavy metal cations for deep treatment,\textsuperscript{28-30} their practical applications are
hindered by the interference from coexisting substances like dissolved organic carbon
(DOC) and salts.\textsuperscript{31, 32}

Very recently, we observed that carboxyl ligands such as gallic acid (GA), tannic
acid (TA), and humic acid (HA) intensively competed for active sites of hydrated
zirconium oxide (HZO) nanoparticles (NPs) with the target pollutant, \textit{i.e.}, phosphate
and fluoride,\textsuperscript{33-36} suggesting the specific interaction between carboxyl ligands and HZO
NPs. Similarly, other studies demonstrated that organic acids like oxalic acid could
greatly enhance adsorption capacity of iron oxides toward Ni(II) through the formation
of Fe-carboxyl-Ni ternary complex.\textsuperscript{37} On the other hand, to address the inherent
drawbacks of NPs such as their tendency to undergo aggregation, operational
challenges associated with the separation of NPs after reaction, and potential release of
NPs into the environment, researchers developed various polymer nanocomposites
(PNCs) by encapsulating active NPs into commercially available, millimeter-sized and
macroporous cross-linked polystyrene (PS) beads.\textsuperscript{38-41} The resultant PNCs integrate the
high adsorption reactivity of NPs with the easy operation of PS hosts, representing one
of the few nanomaterials that have been manufactured in ton-scale and successfully
applied in pilot water treatment.\textsuperscript{42}

Inspired by the above results, here we propose a new strategy to remove heavy
metal-carboxyl complexes from high-salinity water by utilizing the specific interaction
between carboxyl ligands and PNCs. HZO-201, one commercially available PNC
prepared by embedding HZO NPs into a quaternary ammoniated PS beads D201, is
employed to adsorb Cu-citrate complex (a representative heavy metal-carboxyl
complex) from high-salinity water (1.5 % NaCl, w/v). Spectroscopic analyses including
ATR-IR, XPS, and UV-vis confirm the formation of ternary complex between HZO
NPs, citrate, and Cu(II). The exhausted HZO-201 can be readily regenerated with a
binary HCl-NaCl solution during which Cu-citrate complexes decompose into free Cu$^{2+}$,
which are repulsed by the positively charged groups in D201 host, and citrate acid. Column adsorption using a synthetic high-salinity wastewater demonstrates the superior decontamination capability of HZO-201 (~1150 bed volume, BV) over the D201 host (60 BV) and a commercially available cation exchanger D001 (10 BV). Also, HZO-201 exhibits satisfactory adsorption toward Cu(II) complexes with some other carboxyl ligands such as oxalate, tartrate, and succinate. This study provides a reliable solution for efficient removal of heavy metal complexes from high salinity wastewater.

EXPERIMENTAL SECTION

Chemicals and Materials. All the reagents used in this study were of analytical grade unless specified otherwise. ZrOCl$_2$·8H$_2$O was purchased from Aladdin (Shanghai, China). The polymer exchangers D201 and D001, i.e., macroporous polystyrene beads covalently bonded with quaternary ammonium groups and sulfonic groups respectively, were obtained from Zhengguang Industrial Co. Ltd. (Hangzhou, China). The nanocomposite HZO-201 was kindly provided by Jiangsu NJU Environmental Technology Co. Ltd. (Nanjing, China), and the elemental content of Zr in HZO-201 was determined as 6.56% in mass. The pictures of HZO-201, D201 and D001 can be found in Figure S1a. The STEM-HAADF image and basic properties of HZO-201 could be found in Figure S1b and Table S1, respectively. XRD pattern in Figure S2a suggests that the embedded NPs are mainly present in the amorphous phase, and SEM-EDS result in Figure S2b indicates a uniform distribution of HZO on the cross-section of HZO-201 bead. Size distribution of HZO NPs was obtained by statistical analysis on 200 particles randomly selected from TEM photo of HZO-201 in Figure S3a, indicating an average diameter of ~12 nm (Figure S3b). Other chemicals were supplied from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Cu(II) and citrate stock solutions were prepared by dissolving Cu(NO$_3$)$_2$·3H$_2$O and Na$_3$C$_6$H$_5$O$_7$·2H$_2$O with ultrapure water (18.25 MΩ·cm).

Batch adsorption. The batch adsorption assays were carried out at 298K with the dosage of HZO-201 as 0.5 g/L unless specified otherwise. The reaction solutions were prepared by mixing Cu(II) and citrate stock solutions in molar ratio of 1:1, and all
solutions mentioned below are added with 15 g/L NaCl unless otherwise stated. To initiate batch adsorption, the adsorbents were added into 150 mL flask containing 50 mL solution and oscillating for 24 hours in an incubator shaker to achieve adsorption equilibrium, and the solutions were sampled for analysis at time intervals. Solution pHs were maintained at preset values by using 0.1 M HCl or NaOH solution at time intervals.

The exhausted HZO-201 beads were treated by binary HCl (0.01 M)-NaCl (5%, w/v) solution for 24 h to regenerate their adsorption capability toward heavy metal complexes, and then were added into Cu-citrate complex solution to start cyclic adsorption runs. The amounts of Cu-citrate uptake onto the solid adsorbents were calculated according to mass balance.

**Column adsorption.** The fixed-bed adsorption assays were carried out in a glass column (130mm in length and 12 mm in diameter) filled with 5 mL wet adsorbents. The simulated high-salinity wastewater from precipitation units containing Cu-citrate (1 mg Cu/L), 4 g/L Cl\(^{-}\) and 5 g/L SO\(_4^{2-}\) was pumped up-to-down through the adsorbent columns in a constant rate of 10 bed volume (BV) per hour.

**Characterizations and analysis.** The concentration of Cu was determined by atomic absorption spectroscopy (AAS-7000, Shimadzu, Japan). Citrate concentration was estimated by total organic carbon analyzer (TOC-L, Shimadzu, Japan). The surface area and porous structure of HZO-201 was measured by N\(_2\) adsorption–desorption test at 77 K on a Micromeritics Instrument (Nova 3000, Quantachrome). The elemental distribution along the diameter of the cross section of HZO-201 was analyzed by a scanning electron microscope (SEM, HITACHI, S-3400N) equipped with energy dispersive spectrometry (EDS). Scanning TEM (STEM) was performed to get high angle annular dark field (HAADF) images.

Chemical structure of the solid adsorbents was investigated by using *in situ* ATR-FTIR spectroscopy on a Spectrum GX spectrophotometer (Perkin Elmer, USA) with 64 scans at a resolution of 4 cm\(^{-1}\) in the ranging of 4000-525 cm\(^{-1}\). ATR-FTIR spectra of the solid adsorbents were recorded at time intervals after mixing the samples with several droplets of solution containing Cu-citrate complex and 15 g/L NaCl. Laser
excitations were achieved at 532 nm. The interaction between Cu(II)-citrate and HZO was also probed by X-ray photoelectron Spectrometer (XPS) equipped with an Al Kα radiation source (1486.6 eV). Binding energies were corrected using the neutral C 1s peak at 284.8 eV to compensate for the surface charging effects and systematic errors.

RESULTS AND DISCUSSION

**Batch Adsorption of Cu Complex.** Effect of solution salinity on adsorption of Cu-citrate complex by various adsorbents, including HZO-201, D201, and a commercially available PS-based cation exchanger D001 (modified with sulfonic groups), are depicted in Figure 1a. The adsorption capacities of HZO-201 and D201 are both around 2.0 mg Cu/g in absence of NaCl, while negligible Cu-citrate is adsorbed by D001. Such results are expected since Cu-citrate complexes are mainly present in the form of anions at the molar ratio of 1:1, thereby capable of interacting with D201 or HZO-201 through electrostatic attraction. With NaCl concentration increasing to an elevated level (25 g/L), the adsorption capacity of HZO-201 toward Cu-citrate still retains around 0.8 mg Cu/g despite that the electrostatic attraction between Cu-citrate and D201 is almost completely screened. Thus, adsorption of Cu-citrate by HZO-201 at high salinity is mainly attributed to the embedded HZO NPs. For comparison, adsorption isotherms of HZO-201, D201 and D001 toward Cu-citrate in absence of NaCl are illustrated in Figure S5. Clearly, adsorption capacity of D001 is much lower than the other two adsorbents, meanwhile the adsorption of HZO-201 and D201 are very similar with each other. The above results suggest that electrostatic attraction (ion exchange) is the main mechanism for Cu-citrate adsorption onto the solid adsorbents under low salinity condition. Effects of Ca$^{2+}$ on adsorption of Cu-citrate by HZO-201, D201 and D001 are illustrated in Figure S4, from which one can see that >67% adsorption capacity of HZO-201 is retained even Ca$^{2+}$ concentration achieves 1.0 g/L. As described in Figure 1b, adsorption of Cu-citrate by HZO-201 achieves the equilibrium within 1400 min, exhibiting an equilibrium adsorption capacity of 1.78 mg Cu/g and a pseudo-second order rate constant of 0.0016 g/(mg · min$^{-1}$) (See
supplementary Text S1). As expected, the amounts of Cu-citrate uptake onto the ion exchangers, i.e., D201 and D001 are nearly zero. Solution salinity remains constant during adsorption (Figure S6). Adsorption isotherm of Cu-citrate by HZO-201 is depicted in Figure 1c. Clearly, equilibrium adsorption capacities \(Q_e\) of HZO-201 are well fitted by Langmuir model (See supplementary Text S2), possessing a maximum adsorption capacity \(Q_{\text{max}}\) of 8.42 mg Cu/g (~130 mg Cu/g-Zr) and a bind constant \(K_L\) of 0.28 L/mg. Even these values are obtained at high salinity (15 g/L NaCl) and using Cu-citrate complex as the target pollutant, they are still comparable with those of other outstanding adsorbents utilized for decontaminating water from free heavy metal cations.\(^{45,46}\)

Effect of pH on adsorption of Cu-citrate by HZO-201, D201 and D001 are exhibited in Figure 1d. Obviously, adsorption capacity of HZO-201 ascends dramatically with increasing solution pH to ~6, and it is further enhanced by increasing solution pH to ~9. Note that adsorption capacity of HZO-201 declines to nearly zero when pH ≤ 3, implying that acidic treatment might be a promising way to regenerate the exhausted adsorbent for repeated use, as described below. Consistent with the above results, negligible adsorption toward Cu-citrate is observed for D201 and D001 at any pH value. The underlying mechanism for pH effect on adsorption will be further discussed below.

**Adsorption mechanism.** A series of experiments are carried out to probe the underlying adsorption mechanism of Cu-citrate by HZO-201. After adsorption, the molar ratio of residual Cu(II) to citrate ligand (estimated based on dissolved organic carbon, DOC) in solution is always maintained around 1.0 regardless of initial Cu-citrate concentration (Figure 2a), implying that Cu-citrate complex is removed from water as a whole. We also compare UV-vis spectra of the solution after adsorption (residual Cu is 8.10 mg/L) and Cu-citrate complex solution containing the same amount of Cu. As is vividly depicted in Figure 2b, the two spectra are highly overlapped, again suggesting the removal of Cu-citrate as a whole. Theoretically, Cu-citrate complex may interact with HZO-201 through the Cu(II) moiety or the citrate moiety as the anchor.
The results in Figure 2c and 2d show that increasing concentration of citrate ligand results in considerable decline of adsorption capacity toward Cu(II), whereas change of Cu(II) concentration exhibits negligible effect on adsorption of citrate ligand by HZO-201. Thus, we hypothesize that the citrate moiety instead of the Cu(II) moiety plays a key role in the adsorption of Cu-citrate complex by HZO-201, as elucidated below.

After adsorption, HZO-201 sample is analyzed by STEM-EDS. Clearly, the elemental distribution of Zr is highly overlapped with Cu (Figure 3a), suggesting that the adsorption of Cu-citrate by HZO-201 is mainly attributed to the embedded HZO NPs. Similar conclusion can be drawn according to elemental distribution along the cross section of HZO-201 (Figure S2b). During adsorption, *in-situ* ATR-FTIR spectra of HZO-201 are collected at time intervals (Figure 3b). The adsorption bands at 1487 cm\(^{-1}\) and 1479 cm\(^{-1}\) correspond to the vibration of benzene ring, and the band at 1241 cm\(^{-1}\) is assigned to the stretching vibration of C-N.\(^{47, 48}\) These bands stem from the polystyrene skeleton and quaternary ammonium groups of D201 host, respectively. Clearly, no obvious change takes place on the characteristic peaks of D201 host, indicating that electrostatic attraction between D201 host and Cu-citrate complex is almost screened completely at high salinity. Along with the uptake of Cu-citrate complex, the peak at 1045 cm\(^{-1}\) ascribed to the bending vibration of Zr-OH diminishes gradually and eventually vanishes at 10 min. The disappearance of Zr-OH indicates that ligand exchange between hydroxyl group and Cu-citrate complex may be the main mechanism involved in the adsorption of HZO-201 nanocomposite. The evolution of ATR-FTIR spectra also indicates the predominant role of citrate moieties in the adsorption of Cu-citrate complex by HZO-201. When metal oxides (e.g., HZO or iron oxide) form coordination structure with heavy metal cations, oxygen atom serves as the bridge (e.g., Zr-O-Cu),\(^4\) during which the characteristic peak around 1045 cm\(^{-1}\) corresponding to hydroxyl group (-OH) is expected to experience a redshift,\(^{49, 50}\) which is not observed here.

As mentioned above, the embedded HZO NPs are responsible for the adsorption of Cu-citrate complex on HZO-201. We thus prepared unsupported HZO NPs and mixed them with Cu-citrate complex to further probe the adsorption mechanisms. Some
new peaks in the range from 1345 cm$^{-1}$ to 1600 cm$^{-1}$ and around 1033 cm$^{-1}$, which are assigned to the characteristic bands of -COOH, which appear in the ATR-FTIR spectrum of HZO sample during adsorption process (Figure 3c), validating the uptake of Cu-citrate complex. Consistent with these above results, the peak at around 1045 cm$^{-1}$ assigned to the vibration of Zr-OH diminishes over time. Similar phenomenon can be also observed in XPS Zr 3d spectra (Figure S7), where the binding energies of Zr 3d (181.9 eV and 184.3 eV) remain unchanged after Cu(II) adsorption, while a significant shift (0.3 eV) takes place after citrate or Cu-citrate complex uptake.

According to the above results, the removal mechanism of Cu-citrate complex by HZO-201 is schematically illustrated in Figure 4. In brief, a stable ternary complex (Zr-citrate-Cu) forms among the embedded HZO NPs, citrate and Cu(II) using citrate ligands as bridge through ligand exchange between Cu-citrate complexes and surface hydroxyl groups (-OH) of HZO NPs. The formation of Zr-citrate-Cu ternary complex is highly specific and unaffected even at high salinity conditions (e.g., ~1.5%, w/v). In addition to serving as the host, the positively charged D201 plays an important role in regeneration of the exhausted HZO-201 nanocomposite, as elucidated below.

**Potential for practical application.** After adsorption, the exhausted HZO-201 adsorbents are regenerated by binary HCl (0.01M)-NaCl (5%, w/v) solution. The underlying mechanism for generation of HZO-201 is schematically illustrated in Figure 4. The species evolution of Cu-citrate complex as a function of pH is predicted by Visual Minteq 3.1 software. With decreasing pH below 2, Cu(II) moieties in Cu-citrate complexes are replaced by massive protons, transforming the complexes into the mixture of Cu$^{2+}$ cations, citric acid molecules (H$_3$-citrate) and a tiny amount of H$_2$-citrate$^{-}$ anions (Figure S8). Similarly, the interaction between citrate and HZO NPs is greatly suppressed by massive protons, and thus citrate ligands are released from HZO NPs. The net surface charge $Q_H$ (mmol/g) calculated according to previous study represents the net amount of H$^+$ ($Q_H>0$) or OH$^-$ ($Q_H<0$) on the surface of HZO NPs. As suggested in Figure S8c, the point of zero electric charge (pH$_{zpc}$) of HZO-201 is around 5.5, thus the embedded HZO NPs turn into positively charged (-OH$_2^+$) at acidic conditions. As a result, Cu$^{2+}$ cations are repelled by the embedded HZO NPs and the
positively charged D201 host due to electrostatic repulsion. During five-cyclic successive adsorption-regeneration assay, the adsorbed Cu is almost 100% desorbed from HZO-201 (data not shown) and adsorption capacity of the solid sample remains constant (Figure 5a), indicating excellent reusability of the nanocomposite adsorbents. Besides, negligible loss of elemental Zr is observed during repeated use of HZO-201 (Figure 5b), consistent with previous studies. The mechanical strength of HZO-201 was examined by a particle crack device according to previous study. The maximum compressive pressure obtained on the samples before and after 5-cyclic adsorption-regeneration runs are 6.0±0.8 and 8.8±2.2 N (data not shown), indicating that the repeated use exhibits negligible effect on the mechanical strength of HZO-201. After repeated use, the crystalline structure (Figure S2a) and NPs morphology (Figure S9) of HZO-201 are almost the same with the fresh ones, implying outstanding stability of the nanocomposite adsorbent.

Two other nanocomposites, i.e., HZO-001 and HZO-CMPS are prepared by encapsulating HZO NPs inside cation exchanger D001 (modified with sulfonic group) and chloromethylated polystyrene (CMPS, modified with electroneutral chloromethyl group), respectively. The three nanocomposites including HZO-201, HZO-001 and HZO-CMPS are tested in cyclic adsorption-regeneration runs toward Cu-citrate complex. As shown in Figure S10a, the adsorption of HZO-CMPS is inferior to HZO-201 and HZO-001, while the capacity of HZO-001 declines greatly in the second run, mainly arising from the poor desorption efficiency (Figure S10b). Clearly, the quaternary ammonium groups in D201 host play an important role in adsorption of heavy metal complexes and efficient regeneration of the exhausted nanocomposite adsorbent.

To investigate the applicability of HZO-201 in the removal of Cu(II)-citrate complex from high-salinity wastewater, fix-bed column operation is conducted, where HZO-201 adsorbents are packed in the column. Detailed composition of the synthetic feeding solution is available in Figure 6. The emission standard in China (GB21900-2008) sets the MCL value of Cu(II) in industrial effluents as 0.5 mg/L. The HZO-201 column is able to continuously produce ~1150 bed volume (BV) clean water containing
Cu(II) below 0.5 mg/L, while the values for ion exchangers D201 and D001 are ~60 BV and ~10 BV, respectively. As discussed above, once the adsorption capability of HZO-201 is exhausted, they could be fully regenerated by using binary HCl-NaCl solution for next cyclic adsorption run with constant removal efficiency (Figure 5a). For comparison, the synthetic solution is precipitated by Ca(OH)$_2$ and NaOH (precipitation pH ~10.0), respectively, and the residual Cu still retains around 1.0 mg/L (data not shown).

In addition, Cu(II) complexes with other common organic ligands such as oxalate, succinate, tartrate and EDTA are employed to probe removal capability of HZO-201. As suggested in Figure 7, HZO-201 exhibits superior adsorption toward Cu-carboxyl complexes (oxalate, succinate and tartrate complexed Cu) over ion exchangers (D001 and D201), demonstrating the effectiveness of HZO-201 for selective adsorption of various heavy metal-carboxyl complexes from high-salinity water. As for monocarboxyl ligands such as formate, acetate and propionate, they are incapable of forming stable complexes with Cu(II) due to relatively weak complexation capability, as confirmed by the effective removal of Cu(II) by cation exchanger D001 in monocarboxyl systems (Figure S11a), and by the species evolution predicted by Visual Minteq 3.1 software (Figure S11b). Cu-EDTA, Cr-citrate and an electroplating wastewater (after precipitation, Cu ~0.8 mg/L) are treated by D201, D001 and HZO-201. As evidenced by Figure S12, the three adsorbents exhibit poor removal toward Cu-EDTA, possibly due to the cage-like structure of Cu-EDTA complex. As for Cr-citrate and the electroplating wastewater, the adsorption capacities of HZO-201 are much higher than the ion exchangers D201 and D001, implying the great potential of HZO-201 in practical wastewater treatment.

Supporting Information
Supplementary Text S1-S2, Table S1 and Figure S1-S12.

ACKNOWLEDGEMENTS
We greatly appreciate the financial support from National Key R&D Program of China (Grant No. 2017YFE0107200), Major Science and Technology Program for Water Pollution Control and Treatment (Grant No. 2017ZX07204001), Natural Science Foundation of China (Grant No. 21707067) and Jiangsu Province (Grant No. BK20160648)
REFERENCES


(33) Lin, B.; Hua, M.; Zhang, Y. Y.; Zhang, W. M.; Lv, L.; Pan, B. C. Effects of organic acids of different molecular size on phosphate removal by HZO-201 nanocomposite. *Chemosphere* 2017, 166,


(49) Chang-Yan, C.; Jin, Q.; Wen-Sheng, Y.; Jun-Fa, Z.; Zi-Yu, W.; Wei-Guo, S. Low-cost synthesis of


Figure 1. Adsorption of Cu-citrate by HZO-201, D201 and D001 (a) effect of NaCl concentration, pH 7.0 (b) adsorption kinetic of Cu, pH 7.0, (c) adsorption isotherms of Cu, pH 7.0 and (d) adsorption of Cu-citrate as a function of pH. Solid dosage: 0.50 g/L, 298 K.
Figure 2. (a) Molar ratio of residual Cu to citrate in the Cu-citrate solution after adsorption, (b) UV-vis spectra of the Cu-citrate solution after adsorption, and the simulated Cu-citrate solution containing the same amount of Cu, (c) adsorption of Cu(II) as a function of molar ratio (citrate/Cu), and (d) adsorption of citrate by HZO-201 as a function of molar ratio (Cu/citrate). Solid dosage: 0.50 g/L, pH 7.0, 298 K.
Figure 3. (a) STEM-HAADF image of Cu-citrate loaded HZO-201 and the corresponding EDS elemental maps (the red square represents the region of interest, and the yellow square is the background), and in situ ATR-FTIR spectra of (b) HZO-201 and (c) un-supported HZO during adsorption of Cu-citrate at pH 7.0, 298 K.
Figure 4. Schematic illustration for the adsorption of Cu-citrate by HZO-201 and the regeneration of the exhausted HZO-201
**Figure 5.** (a) Cyclic adsorption-regeneration of HZO-201 in batch mode. (Contacting with binary HCl (0.01 M)-NaCl (5%, w/v) solution for 24 h prior to the next adsorption assay), and (b) Leachate of elemental Zr from HZO-201 during cyclic use.
Figure 6. Decontamination of simulated electroplating effluents from Cu-citrate complex by using three separate columns packed with HZO-201, D201 and D001, respectively.
Figure 7. Adsorption of Cu complexes with other carboxyl ligands by HZO-201 ($Q_e$ was expressed in Cu mass, solid dosage: 0.50 g/L, pH 7.0, 298 K)