1 **Effects of Organic Acids of Different Molecular Size on**
2 **Phosphate Removal by HZO-201 Nanocomposite**

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ABSTRACT

Various organic acids in wastewater effluent could significantly influence the performance of phosphate adsorbent. This study focused on the effects of organic acids of different-molecular-size on phosphate adsorption by a novel nanocomposite HZO-201. Three organic acids (gallic acid (GA), tannic acid (TA) and humic acid (HA)) with distinct molecular size ($HA > TA > GA$) were chosen for this purpose. Both isotherm and kinetic tests of phosphate adsorption were conducted in the single-phosphate and binary system, and a series of microscopic techniques (i.e., XPS, FT-IR and SEM-EDX) and N_2 adsorption-desorption test were employed to explore the underlying mechanism. It was found that GA could greatly weaken phosphate adsorption capability of HZO-201 by directly competing for ammonium group on the nanocomposite, TA exhibited significant inhibition on phosphate adsorption rate mainly through pore constriction/blockage, while HA posed negligible impact on phosphate adsorption because of the size exclusion effect. It was also observed that although GA, TA and HA showed substantial influence on bulky HZO due to complexation, their impact on the nano-HZO loaded inside HZO-201 was little. The covalently bounded ammonium group and the networking pore structure of HZO-201 may play important roles in it.

Keywords: Phosphate; Adsorption; Organic acids; Nanocomposite; Molecular size.

1. Introduction

Excessive release of phosphorus into water body has frequently caused undesirable eutrophication on a global scale (Schelske, 2009). Currently, varieties of techniques have been proposed for enhanced removal of phosphate from municipal wastewaters (Mino et al., 1998; Sherwood and Qualls, 2001; Loganathan et al., 2014). Among them, adsorption has been extensively focused on due to its prominent efficiency of phosphorus separation as well as simple operation, low running costs, and potential of phosphorus recovery. But conventional sorbents exhibit inferior selectivity for adsorption toward phosphate over coexisting inorganic species including SO_4^{2-} , NO_3^- , Cl^- and HCO_3^- (Acelas et al., 2015). Thus, various new-type adsorbents have been developed for selective removal of phosphate from secondary effluent (Mullan et al., 2006; Wilsenach et al., 2007; Saha et al., 2009; Zhang et al., 2016). Among them, metal hydroxide-based nanocomposites were drawing ever-increasing attentions in wastewater treatment (Pan et al., 2009; Pan et al., 2014; Chen et al., 2015). Typically, this type of nanocomposites could be synthesized by embedding metal oxide nanoparticles into the inner pores of anion exchange resins. The obtained materials possess two types of adsorption sites for phosphate removal, the ammonium groups covalently bounded onto the polymeric matrix of the host and the loaded metal oxides nanoparticles. The ammonium group could facilitate pre-concentration and permeation of phosphate inside the nanocomposites, and the loaded metal hydroxide nanoparticles could specifically adsorb phosphate mainly through inner-sphere complexation (Chen et al., 2015). This series of nanocomposites showed superior selective adsorption toward phosphate than conventional sorbents in the presence of coexisting anions at high levels, and some of them have been successfully applied in pilot-scale treatment plants for phosphorus removal and water purification.

However, the fact cannot be ignored is that besides the above-mentioned inorganic anions, organic matters also coexist with phosphorus in natural water body and municipal sewage treatment effluent (Kim et al., 2015). It has been confirmed that

the organic matters caused notable impact on the performance of phosphate adsorbents, such as capacity loss and fouling (Beril Gönder et al., 2006; Abrams, 1982). Specifically, the organic acids (i.e., humic acid, tannic acid, gallic acid) which account for 14-60% (in mass) of organic matters in WWTP bio-effluents (Kim and Dempsey, 2008, 2010, 2012), obviously disturb the separation of phosphate from water (Kim, 2015). Compared with other categories of organic matters in effluent, organic acids were preferentially sequestered by adsorbents such as ion exchange resins (Chen et al., 2002) and MIEX[®] magnetic resins (Kim et al., 2015; Kim, 2015) during phosphate separation from secondary effluent. The strong-base anion exchanger exhibited 15-20% capacity losses in gallic acid (GA) or tannic acid (TA) containing solutions during the column cycling tests (Abrams, 1982). Another study revealed GA or TA molecules decreased the adsorption capacity of nitrate-nitrogen onto D201 resin (Song et al., 2013). The co-existed humic acid (HA) was found to expose a slight capacity drop of phosphate onto La-201 according to a latest study (Zhang et al., 2016). These organic acids abundant in aromatic carboxyl or phenolic groups yielded remarkable impact on inorganic anions sequestration by resins, ascribed to their high affinity to the positively charged ammonium groups of resin (Abrams, 1982; Song et al., 2013).

Available studies revealed that molecular size of organics might be a significant factor referring to the influence on adsorptive removal of anion pollutants from water. Organic matters with certain molecular size could permeate into inside pore channels of adsorbents to block the inner pores (Zietzschmann et al., 2014). Li et al. (2003a) discovered that dissolved organic matters with smaller molecular size decreased adsorption capacity of particle active carbon towards atrazine through direct site competition, while those with larger molecular size affected the adsorptive kinetics through pore constriction/blockage. It was also considered that the decrease of micropore volume of active carbon was mainly due to adsorption of the smaller organic molecules, whereas the pore constriction/blockage was primarily resulted from larger molecules occupying mesopore area (Pelekani and Snoeyink, 2001). But contrarily, the inconsistent results also had been drawn that larger TA molecule

exhibited more blockage in micropores of black carbon, while the smaller GA posed no apparent impacts on both micro- and mesopores (Qiu et al., 2009). In addition to the influence of adsorbents' pore structure, organic matters diffusing inside the sorbents could occupy the active sites. For instance, some weak organic acids such as GA and TA could compete for quaternary ammonium groups of strong-base anion resins by aromatic acidic groups of organic acids, and lead to a dramatical decrease of capacity towards NO_3^- anions (Song et al., 2013).

One side, although the effect of molecular size of organic acids on structural characteristic and adsorptive ability of sorbents have been examined aiming for removal of some anionic pollutants, the influence on phosphate sequestration from water is still not clarified. On the other hand, available studies only focused on the traditional sorbents with single active site, such as ion exchange resin and active carbon. Similar investigation on metal hydroxide-resin hybrid adsorbents with unique composite structure is scarce. During our pilot trial of water purification with metal hydroxide-resin hybrid adsorbents, the reduction of organic matters was concurrently observed when phosphate removed (Yang et al., 2015). Therefore, to further improve the efficiency of phosphate sequestration by the hybrid materials, it is necessary to reveal the impact and intrinsic mechanism of organic acids with different molecular size on adsorption of phosphate.

In this research, a lately developed nanocomposite HZO-201 was employed as sorbents for phosphate adsorption. HZO-201 features cross-linked polystyrene supporting matrix covalently bonding ammonium groups and impregnated HZO nanoparticles. HZO-201 has been proved effective for phosphate removal when high-level inorganic anions coexisted (Chen et al., 2015). Three kinds of organic acids, HA, TA and GA, were chosen to evaluate their affection on adsorption of phosphate onto HZO-201 in view of their wide distribution in secondary effluents and marked difference in molecular size. Batch experiments in separated or binary system were conducted to test the effects of the three organic acids on phosphate adsorption by HZO-201. Spectroscopy method was employed for mechanism analysis.

116 **2. Materials and method**

117 **2.1. Materials**

118 All chemicals involved in this study were of analytical grade. $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, GA,
119 TA and HA (sodium salts) were all purchased from Sigma-Aldrich (USA). The
120 structural formulas of the organic acids were described in Fig. S1. The polymer host
121 D201, a macroporous strongly basic anion exchanger, was supplied by Zhengguang
122 Industrial Co., Ltd. (Hangzhou, China). The diameter of D201 beads were in the range
123 of 0.6~0.8 mm. Prior to use, D-201 was subjected to extraction with ethanol in a
124 Soxhlet apparatus to remove possible residual impurities. The aqueous stock
125 containing 1000 mg P/L was prepared by dissolving predetermined KH_2PO_4 into
126 deionized water (18.25 $\text{M}\Omega\cdot\text{cm}$). Desired amount of GA (TA or HA) were also
127 separately dissolved with deionized water to obtain the stock solution of 1000 mg
128 TOC/L.

129 **2.2. Preparation and characterization of nanocomposite adsorbents**

130 The hybrid adsorbent HZO-201 was synthesized by means reported in our
131 previous study (Pan et al., 2013). In brief, 25 g of polymeric host D201 was added
132 into mixed solution of ethanol, HCl and $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, subsequently stirred for 12 h
133 continuously. The Zr(IV) saturated D201 were filtered out and transferred into 200
134 mL of 10 wt % NaOH solution with continuous stirring for another 12 h. The resultant
135 beads were then immersed in 1.0 M NaCl solution to convert the residual OH^- into Cl^- .
136 Finally, the HZO-201 composites were obtained after air-drying at 333 K for 12 h.

137 HZO-201 beads preloaded with organic acids were sampled at the initial GA (TA
138 or HA) concentration of 20 mg TOC/L. The beads were rinsed with distilled water for
139 several times and subsequently vacuum-dried for a week at 323 K. Losses of organic
140 acids after rinse were negligible. Both fresh and loaded HZO-201 were examined for
141 their specific surface area and pore size distribution by N_2 adsorption-desorption tests
142 at 77 K (Micromeritics ASAP-2010C Instrument, Norcross, GA). Standard
143 Brunauer-Emmett-Teller model was employed to calculate the surface area (S_{BET}) of
144 the samples. Micropore and mesopore distributions were analyzed by

145 Horvath-Kawazoe (HK) and Barrett-Joyner-Halendar (BJH) methods, respectively.
146 Besides, the contents of Zr(IV) loaded within HZO-201 composites were detected by
147 inductively coupled plasma atomic emission spectrometry (ICP-AES, PerkinElmer,
148 USA) after nitric-perchloric acid digestion.

149 **2.3. Batch adsorption experiments**

150 In all batch experiments, the dosages of HZO-201 were set as 0.50 g/L. Desired
151 amount of adsorbents were equilibrated in 250 mL flasks containing 100 mL
152 phosphate solution with certain concentration gradients. To investigate the
153 competitive effects of organic acids on phosphate uptake, GA, TA or HA were spiked
154 into solution at desired DOC level, respectively. The mixed solutions were adjusted to
155 pH 6.5 ± 0.2 with NaOH and HCl, then shaken in incubator shakers under 180 rpm at
156 298 K for 7 d (as suggested by preliminary kinetic test) to reach the equilibrium.
157 Kinetic studies were conducted in 1000 mL flasks containing 500 mL phosphate
158 solution with or without organic acids, and 1.0 mL aliquot was sampled at various
159 time intervals for phosphate analysis. The amount of phosphate (or organic acids)
160 captured onto HZO-201 was determined based on mass balance as follows:

$$161 \quad q = (C_0 - C_1) \cdot V/M \quad (1)$$

162 Where q (mg/g) is the amount of adsorbed phosphate (or organic acids), C_0 (mg/L or
163 mg TOC/L) and C_1 (mg/L or mg TOC/L) are the phosphate (or organic acids)
164 concentration before and after adsorption, respectively. V (L) and M (g) separately
165 represent the solution volume and the dosage of adsorbent.

166 **2.4. Analysis**

167 Phosphate concentration was determined by molybdenum blue method with a
168 UV/vis spectrometer (T6, PGENERAL, China) (Tobey et al., 2003). The
169 concentration of organic acids (GA, TA or HA) was determined by total organic
170 carbon analyzer (TOC-L, Shimadzu, Japan). Scanning electron microscope (SEM)
171 plus energy dispersive X-Ray spectroscopy (EDX) (Hitachi S-3400 II, Japan) was
172 employed to analyze the elemental distribution of a cross-section of HZO-201 beads.
173 Fourier transform infrared (FT-IR) spectra of adsorbents before and after adsorption

were recorded at room temperature on a Spectrum GX spectrophotometer (Perkin Elmer, USA) at a resolution of 2 cm⁻¹. The interaction of phosphate and organic acids on the inner surface of HZO-201 was probed by X-ray photoelectron Spectrometer (XPS, ESCALAB-2, UK) equipped with an Al K α anode as the excitation source. The binding energies were corrected using C1s calibration energy of 284.8 eV. XPS data processing and peak fitting were analyzed through XPSPEAK 41 program (Raymund W.M. Kwok, HongKong, China).

3. Results and discussion

3.1. Characterization of the fresh and preloaded HZO-201

Tabel 1

General characteristics of the fresh or organic-acid-loaded HZO-201.

Sample	L_{OA}^a (mg TOC/g)	S_{BET}^b (m ² /g)	d_{ave}^c (nm)	V_{total}^d (cm ³ /g)	V_{micro}^e (cm ³ /g)	Zr content (wt %)	Particle size (mm)
HZO-201	-	51.30	15.80	0.2027	0.0184		
HZO-201-GA	36.22	46.32	12.62	0.1462	0.0161	15.85	0.6~0.8
HZO-201-TA	12.30	28.93	12.85	0.0930	0.0100		
HZO-201-HA	1.82	57.95	14.84	0.2150	0.0206		

^a Loading rates of organic acids at the initial concentration of 20 mg TOC/L; ^b BET surface area;

^c Average pore diameter; ^d Total pore volume; ^e Micropore volume.

In our study, a novel hybrid nanocomposite HZO-201 was fabricated by impregnating HZO nanoparticles inside macroporous D201 matrix covalently bound with positively charged ammonium groups. The cross-linked porous structures and charged functional groups of the polymeric host was expected to facilitate the dispersion of HZO nanoparticles within the D201 host (Zhang et al., 2013, 2015a). Based on the radial elements distribution of HZO-201 in Fig. 9a (presented in section 3.5), more nano-HZO were encapsulated in the outer region of HZO-201 beads, while the ammonium groups uniformly distributed in cross section of the composites, consistent with the result reported by Zhang et al. (2015b). As shown in Table 1, the

specific surface area of fresh HZO-201 was 51.30 m²/g, with an average pore size of 15.80 nm. The average molecular size of GA, TA and HA were examined to be 0.57 nm, 2.84 nm and 1.2~4 nm respectively, in according to (Table S1) Qiu et al. (2009), Ferro-Garcia et al. (1998) and Lu et al. (2012).

The organic acids with initial concentration of 20 mg TOC/L were adsorbed onto HZO-201 individually. As depicted in Table 1, the loading amount of GA in HZO-201 was 36.22 mg TOC/g, nearly three times more than TA, while the HA loading was only 1.82 mg TOC/g. After TA loading, the S_{BET} and V_{total} of HZO-201 reduced by 43.61% and 54.13%, respectively, suggesting a large amount of pores were blockaded by TA molecules. By contrast, GA loading generated less change in S_{BET} and V_{total} , even at higher loading amounts. This could be attributed to the smaller molecular size of GA than TA and HA. Moreover, the percentage of reduction in $V_{\text{meso/macro}}$ (54.98%) was higher than that in V_{micro} (45.65%) after adsorption of TA onto HZO-201, indicating the pore blockage/restriction was more severe in mesopores than in micropores, which was also verified by the decrease of average pore width.

Fig. 1. Pore-size distribution of fresh and organic-acids-loaded HZO-201 samples: (a) mesopore plots by BJH method. (b) micropore plots by HK method.

As depicted in pore size distributions of the samples (Fig. 1), pores of fresh

216 HZO-201 dominated in mesopores of diameter ranging from 10 to 30 nm. Loading of
 217 organic acids generated distinct variations on pore structure of the nanocomposites.
 218 For TA-loaded sample, the maximum peak position of pore size distribution in the
 219 mesopore range shifted to smaller area, with the peak intensity decreased by 66.51%
 220 (Fig. 1a). On the other hand, the volume of some narrower mesopores (2~10 nm)
 221 increased to some extent, verifying the conversion of large mesopores into smaller
 222 ones, this was in consistent with the decrease of d_{ave} . Loading of GA onto HZO-201
 223 caused similar tendency of mesopores distribution with Loading of TA, but less
 224 decline of peak intensity. By comparison, the changes in pore structure from HA
 225 loading were limited in both micro- (Fig. 1b) and mesopore areas. In short,
 226 accumulation of TA in interior of HZO-201 was the primary contribution to pore
 227 blockage/restriction.

228 3.2. The effect of organic acids concentration on phosphate removal

229
 230 **Fig. 2.** Competing effects of organic acids on phosphate removal (initial phosphate, 10 mg/L;
 231 adsorbent dosage, 0.5 g/L; T, 298 K; initial pH, 6.5 ± 0.2).
 232

233 The effect of organic acids concentration on phosphate adsorption by HZO-201
 234 was illustrated in Fig. 2. When the organic acids were below 10 mg TOC/L, the
 235 removal rates of phosphate remained unchanged. A noticeable decline in phosphate
 236 removal rate was observed when further increasing organic acids concentration to 100
 237 mg TOC/L. The decline rate resulted from co-existed organic acids followed an
 238 increasing order as GA (59.57%)>TA (43.22%)>HA (20.02%). Phosphate removal
 239 reached a plateau when organic acids concentration was above 100 mg TOC/L. It
 240 indicated negligible sites were occupied at low organic acids level and adsorptive sites
 241 were not limited for phosphate adsorption (Tinnacher et al., 2015). However, at higher
 242 concentration, organic acids of small molecular size, e.g. GA and TA, competed
 243 greatly with phosphate for adsorptive sites. It was deduced that the effect of HA was
 244 less prominent because the larger HA molecules were inaccessible to the inner pores
 245 of adsorbents (Zhang et al., 2014). Thus, the molecular size of the organic acids
 246 played a significant role in phosphate sequestration by HZO-201. More detailed
 247 mechanism will be discussed below.

248 3.3. Effect of organic acids on adsorption kinetics

249

250 **Fig. 3.** Kinetics of phosphate adsorption by HZO-201 in the presence and absence of organic acids
251 (initial phosphate, 10 mg/L; initial organic acid, 20 mg TOC/L; adsorbent dosage, 0.5 g/L; T, 298
252 K; initial pH, 6.5 ± 0.2).

253

254 Kinetic profiles of phosphate adsorption in single or binary system were
255 illustrated in [Fig. 3](#). The adsorption equilibrium of phosphate reached within 500 min
256 when no organic acids were present. GA prolonged equilibrium time to over 1000 min,
257 and the equilibrium time was extended to over 8000 min after TA being introduced
258 into the systems. It was found that 7 d were required to reach equilibrium when TA
259 co-existed with phosphate (data not shown). The slower kinetics of phosphate
260 adsorption could be attributed to the changes in pore structure of HZO-201 after
261 organic acids loading. As discussed in [section 3.1](#), TA molecules blocked or
262 constricted a great number of micro- or mesopores, dramatically hindering the
263 diffusion of phosphate into inner pores of HZO-201. Nevertheless, the smaller GA
264 molecules posed less change in this respect. By contrast, the largest HA molecules
265 exhibited negligible impact on phosphate adsorption rate, because of the size
266 exclusion that HA hardly permeated into the pores of HZO-201. Similar results were
267 reported by [Newcombe et al. \(2002\)](#) and [Li et al. \(2003b\)](#).

268 Pseudo-first and -second order kinetic model ([Text S1](#)) were employed to
269 quantitatively analyze the adsorptive kinetics of phosphate under coexistence or
270 nonexistence of organic acids. The fitting parameters were summarized in ([Table S2](#)).

3.4. Effect of organic acids on adsorption isotherms

Fig. 4. Adsorption isotherms of phosphate onto HZO-201 in the presence and absence of organic acids (initial organic acid, 20 mg TOC/L; adsorbent dosage, 0.5 g/L; T, 298 K; initial pH, 6.5 ± 0.2).

The adsorption isotherm of phosphate by HZO-201 in single and binary systems were exhibited in Fig. 4. The adsorption isotherm of P-PO_4^{3-} under the coexistence of HA appeared similar trends as in the single-phosphate isotherm, indicating that HA exerted insignificant impact on phosphate adsorption capacity of HZO-201. The presence of TA reduced phosphate uptake by HZO-201 at low equilibrium P concentration (<10 mg/L), increasing in phosphate concentration diminished the adverse effect of TA. It was possibly because the blocked micropores substantially inhibited the removal of phosphate at low concentration, as the adsorption at low equilibrium concentration was believed to dominantly occur in micropores instead of mesopores (Qiu et al., 2009), whereas the residual mesopores after TA blocking were still sufficient for sequestering phosphate at high level due to the abundance of

mesopore in HZO-201. However, GA remarkably reduced the phosphate adsorption within the identical concentration range. Pelekani and Snoeyink (1999) found that organic matters adsorption mainly occurred in pores larger than 1.7 times molecule's second-widest dimension. Consequently, TA and HA molecules were inaccessible to most micropores (0~2 nm) in consideration of their average size of 2.84 and 1.2~4 nm, respectively (Ferro-Garcia et al., 1998; Lu et al., 2012). Only a small part of sites in mesopores could be occupied by TA or HA molecules. In comparison, GA (with molecular size of 0.57 nm) would occupy more adsorptive sites for their accessibility to both micro- and mesopore areas of HZO-201. For this reason, TA or HA in mesopores exhibited less competing effect on phosphate sequestration due to the preferential adsorption toward phosphate by nano-HZO over the competing organic acids, while a strong competition for amino groups by GA occurred in micropores for the lack of nano-HZO particles in this area. Additionally, Langmuir and Freundlich models (Text S2) were used to fit isotherm data, and the obtained parameters were summarized in Table S3.

3.5. Competing mechanism of organic acids on phosphate adsorption

Fig. 5 Schematic illustration of HZO-201 nanocomposite and its' phosphate sequestration.

306

307 As illustrated in [Fig. 5](#), the hybrid HZO-201 is of a cross-linked porous structure
308 with HZO nanoparticles impregnated inside the macroporous D201 matrix. It features
309 two distinct active sites available for phosphate sequestration, the positively charged
310 quaternary ammonium groups covalently bound with the matrix of D201 and the
311 immobilized HZO nanoparticles inside D201. Phosphate adsorption could be achieved
312 through the nonspecific electrostatic attraction by the host D201 and the specific
313 Lewis acid-base interaction or ligand exchange by HZO nanoparticles ([Chen et al.,](#)
314 [2015](#)). Organic acids were negatively charged that they could easily interact with
315 ammonium groups through ion exchange, and would also interact with metal
316 hydroxide through complexation ([Wang et al., 2010](#); [Pommerenk and Schafran, 2005](#);
317 [Genz et al., 2008](#)). Here, the bulky HZO and polymer-supported nanosized HZO
318 (HZO-201) were both investigated individually to further elucidate the underlying
319 mechanism of competitive adsorption between phosphate and organic acids.

320

321 **Fig. 6.** (a) The phosphate adsorption by bulky HZO with the coexistence of organic acids (initial

322 phosphate, 10 mg/L; adsorbent dosage, 0.5 g/L; T, 298 K; initial pH, 6.5±0.2); (b) XPS spectra of

323 Zirconium before and after adsorbing P or organic acids by bulky HZO.

324 As depicted in [Fig. 6a](#), the phosphate uptake declined with different degrees in
325 organic acid-contained solution, indicating distinct competing effects of the examined
326 organic acids on phosphate removal by bulky HZO. [Fig. 6b](#) demonstrated the surface
327 Zr3d spectra of bulky HZO, phosphate/HZO, and organic acid/HZO, respectively.
328 The binding energy of Zr core line $3d_{5/2}$ (181.93 eV) shifted to 182.30 eV after
329 phosphate, GA or TA adsorption, and it shifted to 182.16 eV after HA adsorption,
330 suggesting that superficial reactions might occur between phosphate or organic acids
331 and zirconium ([Su et al., 2013](#); [Zong et al., 2013](#)). It was likely that binding to
332 phosphate or organic acids caused the loss of electron density at zirconium, which in
333 turn raised the binding energy of Zr $3d_{5/2}$ ([Dou et al., 2012](#)). Therefore, organic acids
334 probably competed the HZO sites by forming chemical bonds with HZO surface sites.

335

336 **Fig. 7.** FT-IR spectra of (a) HZO before and after adsorbing P or organic acids, and of (b) GA

337 before and after being adsorbed onto HZO.

FT-IR spectra of fresh and loaded HZO samples (adsorption of P-PO_4^{3-} or organic acids) were shown in Fig. 7a. The fresh HZO exhibited a strong deformation vibration (1340.28 cm^{-1}) of Zr-OH derived from the hydroxyl present on surface of HZO particles (Liu et al., 2008; Zhang et al., 2013). After phosphate adsorption, the peak of Zr-OH was shifted to a higher wavenumber zone (1374.99 cm^{-1}) and weakened dramatically. Such observation demonstrated the replacement of surface Zr-OH contributed to the phosphate adsorption (Su et al., 2013). The peak appearing at 1013.41 cm^{-1} was assigned to the bending vibration of adsorbed P-PO_4^{3-} (Liu et al., 2008), ascribed to inner-sphere complexes between phosphate and surface hydroxyl groups (Chen et al., 2015). Besides, wavenumber blue shifts of Zr-OH deformation vibration peak occurred after adsorption of organic acids. As depicted in Fig. 7b, the stretching vibration of phenolic groups ($-\text{OH}$, 1241.5 cm^{-1}) and carboxylic groups (C=O , 1538.9 cm^{-1}) of GA were shifted to 1223.6 cm^{-1} , 1502.3 cm^{-1} after adsorption onto HZO, respectively (Kang and Xing, 2008; Yan et al., 2013). These findings explained that carboxylic or phenolic functional groups of organic acids might participate in the ligand exchange with surface hydroxyl groups of HZO (Philippe and Schaumann, 2014). Here, we proposed the competitive mode of organic acids for HZO surface sites as depicted in Fig. S2.

Fig. 8. P2p XPS spectra of phosphate-loaded HZO-201 in the absence and presence of organic acids. Peak A represented phosphorus captured by ammonium groups of D201, and peak B represented phosphorus adsorbed by nano-HZO, S (A) and S (B) referred to the area of Peak A and B, respectively.

To further distinguish the effect of organic acids on phosphate adsorption by two different kinds of active sites in HZO-201, XPS spectra analysis was conducted. As illustrated in Fig. S3, the binding energy of phosphate captured by D201 was observed at 133.05 eV. Higher binding energy of P-HZO at 133.56 eV suggested much stronger P-Zr complexing reaction than nonspecific electrostatic attraction for D201. The P2p XPS spectra of phosphate-loaded HZO-201 in the single phosphate or phosphate/organics binary systems were presented in Fig. 8, with calculated parameters summarized in Table 2. Obviously, the encapsulated nano-HZO exhibited a higher P2p binding energy than bulky HZO, possibly attributed to the larger surface areas and stronger surface reactivity of nano-HZO (Burda et al., 2005; Figueiredo et

al., 2011). What's more, the co-existence of GA caused a large reduction of phosphate sequestered by host D201 from 77.46 to 41.79%, whereas the phosphate captured by nano-HZO increased from 22.54 to 58.21%. It implied that competition between GA and phosphate occurred mainly for the active sites of host D201, while the nano-HZO exhibited a preferential phosphate adsorption over the organic acid molecules. This finding confirmed the more specific affinity between phosphate and nano-HZO (Arai and Sparks, 2001; Chitrakar et al., 2006). By comparison, the TA or HA of larger molecular size generated less disturbance in phosphate uptakes from both the two active sites, verifying that HZO-201 nanocomposites displayed better resistance to organic acids with larger molecular sizes. This was in an agreement with the results of isotherm tests mentioned above.

Table 2

Peak shape fitting parameters for P2p XPS peaks of HZO-201 after phosphate adsorption in the absence or presence of organic acids.

Sample	Peak ^a	B.E. (eV) ^b	Area	FWHM (eV) ^c	Percent (%) ^d
HZO-201-P	P-D201	133.0	207.9	2.05	77.46
	P-HZO	133.7	60.5	2.45	22.54
HZO-201-P (GA)	P-D201	133.0	102.6	2.85	41.79
	P-HZO	133.7	142.9	2.09	58.21
HZO-201-P (TA)	P-D201	133.0	156.2	2.09	68.78
	P-HZO	133.7	70.9	1.62	31.22
HZO-201-P (HA)	P-D201	133.0	213.8	2.09	80.07
	P-HZO	133.7	53.2	1.96	19.93

^a Surface species: P-D201 represents the phosphorus bonded to the ammonium groups of D201, and P-HZO represents that that captured by nano-HZO;

^b Binding energy (B.E.);

^c The full width at half maximum (FWHM);

^d The percentage represents the contribution of each peak to the total number of counts under the P(2p) peak.

Fig. 9. Radial elemental distribution of HZO-201. (a) Zr, P, N, S and Cl distribution after phosphate captured by HZO-201 in the presence of 500 mg/L S-SO_4^{2-} ; (b) Zr, P, N, S and Cl distribution after phosphate captured by HZO-201 in the presence of 500 mg/L S-SO_4^{2-} and 50 mg TOC/L GA.

396 In order to separately explore the phosphate-adsorptive function and the
397 organic-acid-resistant performance of the two types of active sites, 500 mg/L sulfate
398 was introduced into the system to paralyze the ion exchange effect of the host
399 ammonium group. SEM-EDX analysis on HZO-201 beads were conducted to reveal
400 the radial elemental distributions of adsorbed phosphate and sulfur inside adsorbents
401 under the background of organic acid or without. The elemental Zr, N and Cl were
402 also detected in situ to characterize the locations of nano-HZO and ammonium groups
403 inside the nanocomposite beads. Here, GA was selected as the representative because
404 of its highest loading amount comparing with HA and TA. As depicted in Fig. 9a, the
405 distribution of elemental P and S matches well with that of Zr and N respectively,
406 implying nano-HZO and $R-N^+(CH_3)_3Cl^-$ sites preferentially captured phosphate and
407 sulfate through independent binding pathways. After addition of GA, a significant
408 reduction of S and Cl elements were observed in the inner region of HZO-201 beads,
409 while the uniformity of elemental distribution between Zr and P was never changed
410 (Fig. 9b). It could be inferred that the ionized GA exchanged Cl^- of $R-N^+(CH_3)_3Cl^-$
411 through ion exchange, sequentially occupying the adsorptive sites dominated by
412 sulfate. Of note, the affinity of GA for $R-N^+(CH_3)_3$ sites proved to be superior to that
413 of SO_4^{2-} based on analysis above. Therefore, competing for quaternary ammonium
414 groups of HZO-201 was expected to be the major competitive mechanism between
415 organic acids and phosphate. The polymeric host D201 protected the encapsulated
416 nano-HZO particles from complexing with organic acids, overcoming the inferior
417 organic-acid-resistant performance of bulky HZO for phosphate adsorption. Similar
418 findings were also observed in some other studies (Zhang et al., 2016; Shuang et al.,
419 2013).

420 **4. Conclusions**

421 In this study, three organic acids (gallic acid (GA), tannic acid (TA) and humic
422 acid (HA)) with different-molecular-size were chosen to investigate their impacts on
423 phosphate adsorption by HZO-201 nanocomposite. Both isotherm and kinetic tests of
424 phosphate adsorption by HZO-201 were conducted in the single-phosphate or
425 multicomponent system. The small-sized GA was found to reduce the adsorption
426 capacity by directly competing for adsorption sites and relatively larger TA
427 significantly inhibited phosphate adsorption kinetics due to pore constriction/blockage,
428 while HA molecules posed negligible impact on phosphate adsorption because of the
429 size exclusion effects. Interestingly, by employing a series of microscopic techniques
430 (i.e., XPS, FT-IR and SEM-EDX), it was validated that organic acids could occupy
431 Zr-OH sites of bulky HZO through ligand exchange, while posed negligible impacts
432 on encapsulated nano-HZO inside HZO-201. Consequently, competing for quaternary
433 ammonium groups of HZO-201 through ion exchange was expected to be the main
434 competitive mechanism between organic acids and phosphate.

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References

- Abrams, I.M., 1982. Organic fouling of ion exchange resins. *Stud. Environ. Sci.* 19, 213-224.
- Acelas, N.Y., Martin, B.D., Lopez, D., Jefferson, B., 2015. Selective removal of phosphate from wastewater using hydrated metal oxides dispersed within anionic exchange media. *Chemosphere* 119, 1353-1360.
- Arai, Y., Sparks, D.L., 2001. ATR-FTIR spectroscopic investigation on phosphate adsorption mechanisms at the ferrihydrite-water interface. *J. Colloid Interface Sci.* 241, 317-326.
- Beril Gnder, Z., Kaya, Y., Vergili, I., Barlas, H., 2006. Capacity loss in an organically fouled anion exchanger. *Desalination* 189, 303-307.
- Burda, C., Chen, X.B., Narayanan, R., El-Sayed, M.A., 2005. Chemistry and properties of nanocrystals of different shapes. *Chem. Rev.* 105, 1025-1102.
- Chen, J.P., Chua, M.L., Zhang, B.P., 2002. Effects of competitive ions, humic acid, and pH on removal of ammonium and phosphorous from the synthetic industrial effluent by ion exchange resins. *Waste Manage.* 22, 711-719.
- Chen, L., Zhao, X., Pan, B., Zhang, W., Hua, M., Lv, L., Zhang, W., 2015. Preferable removal of phosphate from water using hydrous zirconium oxide-based nanocomposite of high stability. *J. Hazard. Mater.* 284, 35-42.
- Chitrakar, R., Tezuka, S., Sonoda, A., Sakane, K., Ooi, K., Hirotsu, T., 2006. Selective adsorption of phosphate from seawater and wastewater by amorphous zirconium hydroxide. *J. Colloid Interface Sci.* 297, 426-433.
- Dou, X., Mohan, D., Pittman, C.U., Yang, S., 2012. Remediating fluoride from water using hydrous zirconium oxide. *Chem. Eng. J.* 198-199, 236-245.
- Ferro-Garcia, M.A., Rivera-Utrilla, J., Bautista-Toledo, I., Moreno-Castilla, C., 1998. Adsorption of humic substances on activated carbon from aqueous solutions and their effect on the removal of Cr(III) ions. *Langmuir* 14, 1880-1886.
- Figueiredo, N.M., Carvalho, N.J.M., Cavaleiro, A., 2011. An XPS study of Au alloyed Al-O sputtered coatings. *Appl. Surf. Sci.* 257, 5793-5798.
- Genz, A., Baumgarten, B., Goernitz, M., Jekel, M., 2008. NOM removal by adsorption onto granular ferric hydroxide: Equilibrium, kinetics, filter and regeneration studies. *Water Res.* 42, 238-248.
- Kang, S., Xing, B., 2008. Humic acid fractionation upon sequential adsorption onto goethite. *Langmuir* 24, 2525-2531.
- Kim, H.C., 2015. High-rate MIEX filtration for simultaneous removal of phosphorus and membrane foulants from secondary effluent. *Water Res.* 69, 40-50.
- Kim, H.C., Dempsey, B.A., 2012. Comparison of two fractionation strategies for characterization of wastewater effluent organic matter and diagnosis of membrane fouling. *Water Res.* 46, 3714-3722.
- Kim, H.C., Dempsey, B.A., 2008. Effects of wastewater effluent organic materials on fouling in ultrafiltration. *Water Res.* 42, 3379-3384.
- Kim, H.C., Dempsey, B.A., 2010. Removal of organic acids from EfOM using anion exchange resins and consequent reduction of fouling in UF and MF. *J. Membr. Sci.* 364, 325-330.
- Kim, H.C., Timmes, T.C., Dempsey, B.A., 2015. Simultaneous removal of phosphorus and EfOM using MIEX, coagulation, and low-pressure membrane filtration. *Environ. Technol.* 36, 3167-3175.

Li, Q.L., Snoeyink, V.L., Mariaas, B.J., Campos, C., 2003a. Elucidating competitive adsorption mechanisms of atrazine and NOM using model compounds. *Water Res.* 37, 773-784.

Li, Q.L., Snoeyink, V.L., Marinas, B.J., Campos, C., 2003b. Pore blockage effect of NOM on atrazine adsorption kinetics of PAC: the roles of PAC pore size distribution and NOM molecular weight. *Water Res.* 37, 4863-4872.

Liu, H., Sun, X., Yin, C., Hu, C., 2008. Removal of phosphate by mesoporous ZrO₂. *J. Hazard. Mater.* 151, 616-622.

Loganathan, P., Vigneswaran, S., Kandasamy, J., Bolan, N.S., 2014. Removal and recovery of phosphate from water using sorption. *Crit. Rev. Env. Sci. Technol.* 44, 847-907.

Lu, Z., Jiang, B., Li, A., 2012. Investigation of the anti-fouling performance of an aminated resin. *Chem. Eng. J.* 193-194, 139-145.

Mino, T., Van Loosdrecht, M.C.M., Heijnen, J.J., 1998. Microbiology and biochemistry of the enhanced biological phosphate removal process. *Water Res.* 32, 3193-3207.

Mullan, A., McGrath, J.W., Adamson, T., Irwin, S., Quinn, J.P., 2006. Pilot-scale evaluation of the application of low pH-inducible polyphosphate accumulation to the biological removal of phosphate from wastewaters. *Environ. Sci. Technol.* 40, 296-301.

Newcombe, G., Morrison, J., Hepplewhite, C., Knappe, D.R.U., 2002. Simultaneous adsorption of MIB and NOM onto activated carbon - II. Competitive effects. *Carbon* 40, 2147-2156.

Pan, B., Han, F., Nie, G., Wu, B., He, K., Lu, L., 2014. New strategy to enhance phosphate removal from water by hydrous manganese oxide. *Environ. Sci. Technol.* 48, 5101-5107.

Pan, B., Wu, J., Pan, B., Lv, L., Zhang, W., Xiao, L., Wang, X., Tao, X., Zheng, S., 2009. Development of polymer-based nanosized hydrated ferric oxides (HFOs) for enhanced phosphate removal from waste effluents. *Water Res.* 43, 4421-4429.

Pan, B., Xu, J., Wu, B., Li, Z., Liu, X., 2013. Enhanced removal of fluoride by polystyrene anion exchanger supported hydrous zirconium oxide nanoparticles. *Environ. Sci. Technol.* 47, 9347-9354.

Pelekani, C., Snoeyink, V.L., 1999. Competitive adsorption in natural water: Role of activated carbon pore size. *Water Res.* 33, 1209-1219.

Pelekani, C., Snoeyink, V.L., 2001. A kinetic and equilibrium study of competitive adsorption between atrazine and Congo red dye on activated carbon: the importance of pore size distribution. *Carbon* 39, 25-37.

Philippe, A., Schaumann, G.E., 2014. Interactions of dissolved organic matter with natural and engineered inorganic colloids: a review. *Environ. Sci. Technol.* 48, 8946-8962.

Pommerenk, P., Schafran, G.C., 2005. Adsorption of inorganic and organic ligands onto hydrous aluminum oxide: Evaluation of surface charge and the impacts on particle and NOM removal during water treatment. *Environ. Sci. Technol.* 39, 6429-6434.

Qiu, Y., Xiao, X., Cheng, H., Zhou, Z., Sheng, G.D., 2009. Influence of environmental factors on pesticide adsorption by black carbon: pH and model dissolved organic matter. *Environ. Sci. Technol.* 43, 4973-4978.

Saha, B., Chakraborty, S., Das, G., 2009. A mechanistic insight into enhanced and selective phosphate adsorption on a coated carboxylated surface. *J. Colloid Interface Sci.* 331, 21-26.

Schelske, C.L., 2009. Eutrophication: focus on phosphorus. *Science* 324, 722-722.

Sherwood, L.J., Qualls, R.G., 2001. Stability of phosphorus within a wetland soil following ferric chloride treatment to control eutrophication. *Environ. Sci. Technol.* 35, 4126-4131.

Shuang, C., Wang, M., Zhou, Q., Zhou, W., Li, A., 2013. Enhanced adsorption and antifouling performance of anion-exchange resin by the effect of incorporated Fe_3O_4 for removing humic acid. *Water Res.* 47, 6406-6414.

Song, H., Yao, Z., Wang, M., Wang, J., Zhu, Z., Li, A., 2013. Effect of dissolved organic matter on nitrate-nitrogen removal by anion exchange resin and kinetics studies. *J. Environ. Sci.* 25, 105-113.

Su, Y., Cui, H., Li, Q., Gao, S., Shang, J.K., 2013. Strong adsorption of phosphate by amorphous zirconium oxide nanoparticles. *Water Res.* 47, 5018-5026.

Tinnacher, R.M., Begg, J.D., Mason, H., Ranville, J., Powell, B.A., Wong, J.C., Kersting, A.B., Zavarin, M., 2015. Effect of fulvic acid surface coatings on plutonium sorption and desorption kinetics on goethite. *Environ. Sci. Technol.* 49, 2776-2785.

Tobey, S.L., Jones, B.D., Anslyn, E.V., 2003. C-3v symmetric receptors show high selectivity and high affinity for phosphate. *J. Am. Chem. Soc.* 125, 4026-4027.

Wang, J., Zhou, Y., Li, A., Xu, L., 2010. Adsorption of humic acid by bi-functional resin JN-10 and the effect of alkali-earth metal ions on the adsorption. *J. Hazard. Mater.* 176, 1018-1026.

Wilsenach, J.A., Schuurbiers, C.A.H., van Loosdrecht, M.C.M., 2007. Phosphate and potassium recovery from source separated urine through struvite precipitation. *Water Res.* 41, 458-466.

Yan, W., Zhang, J., Jing, C., 2013. Adsorption of Enrofloxacin on montmorillonite: Two-dimensional correlation ATR/FTIR spectroscopy study. *J. Colloid Interface Sci.* 390, 196-203.

Yang, W., Yu, Z., Pan, B., Lv, L., Zhang, W., 2015. Simultaneous organic/inorganic removal from water using a new nanocomposite adsorbent: A case study of p-nitrophenol and phosphate. *Chem. Eng. J.* 268, 399-407.

Zhang, Q., Du, Q., Hua, M., Jiao, T., Gao, F., Pan, B., 2013. Sorption enhancement of lead ions from water by surface charged polystyrene-supported nano-zirconium oxide composites. *Environ. Sci. Technol.* 47, 6536-6544.

Zhang, Q., Du, Q., Jiao, T., Pan, B., Zhang, Z., Sun, Q., Wang, S., Wang, T., Gao, F., 2013. Selective removal of phosphate in waters using a novel of cation adsorbent: Zirconium phosphate (ZrP) behavior and mechanism. *Chem. Eng. J.* 221, 315-321.

Zhang, Q., Du, Q., Jiao, T., Teng, J., Sun, Q., Peng, Q., Chen, X., Gao, F., 2015a. Accelerated sorption diffusion for Cu(II) retention by anchorage of nano-zirconium dioxide onto highly charged polystyrene material. *Sci. Rep.* 5, 10646.

Zhang, M., Li, A., Zhou, Q., Shuang, C., Zhou, W., Wang, M., 2014. Effect of pore size distribution on tetracycline adsorption using magnetic hypercrosslinked resins. *Microporous Mesoporous Mater.* 184, 105-111.

Zhang, Y., Pan, B., Shan, C., Gao, X., 2016. Enhanced phosphate removal by nanosized hydrated La(III) oxide confined in cross-linked polystyrene networks. *Environ. Sci. Technol.* 50, 1447-1454.

Zhang, Q., Teng, J., Zhang, Z., Nie, G., Zhao, H., Peng, Q., Jiao, T., 2015b. Unique and outstanding cadmium sequestration by polystyrene-supported nanosized zirconium hydroxides: a case study. *RSC Adv.* 5, 55445-55452.

Zhang, Q., Teng, J., Zou, G., Peng, Q., Du, Q., Jiao, T., Xiang, J., 2016. Efficient phosphate sequestration for water purification by unique sandwich-like MXene/magnetic iron oxide nanocomposites. *Nanoscale* 8, 7085-7093.

Zietzschmann, F., Worch, E., Altmann, J., Ruhl, A.S., Sperlich, A., Meinel, F., Jekel, M., 2014. Impact

570 of EfOM size on competition in activated carbon adsorption of organic micro-pollutants from
571 treated wastewater. *Water Res.* 65, 297-306.
572 Zong, E., Wei, D., Wan, H., Zheng, S., Xu, Z., Zhu, D., 2013. Adsorptive removal of phosphate ions
573 from aqueous solution using zirconia-functionalized graphite oxide. *Chem. Eng. J.* 221, 193-203.