Supplementary Information

Surface Functionalized Poly(vinyl alcohol)-Hydrous Zirconium Oxide Composite Beads for Efficient and Selective Sequestration of Phosphate from Wastewater

Huayong Luo[a], Mingxuan Zhang [a], Hongwei Rong[a], Zuhao Chen[a], Xueyang Zeng[a], Jingyin Wang[a], Binhua Liu[a], Peng Liao[b*]

[a]School of Civil Engineering, Guangzhou University, Guangzhou, 510006, China

[b]State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, 550081, PR China

*Corresponding authors:

Peng Liao
liaopeng@mail.gyig.ac.cn

Number of Pages: 21

Number of Tables: 5

Number of Figures: 9

Data analysis and modeling

Determination of batch adsorption performance

The equilibrium uptake amount (q_e, mg/g) and the uptake amount (q_t, mg/g) at time t of the adsorbent beads were determined by eqs. (S1) and (S2).

$$q_e = \frac{(C_o - C_e) \times V}{m} \qquad \text{(S1)}$$

$$q_t = \frac{(C_o - C_t) \times V}{m} \qquad \text{(S2)}$$

where C_o (mg/L), C_e (mg/L) and C_t (mg/L) are phosphate concentrations in the aqueous solutions at the initial time, equilibrium time, and time t (min); V is the volume of the aqueous solution (L); and m is the mass of the beads (g).

The desorption efficiency (DE) was determined from eq. (S3).

$$DE = \frac{C \times V}{(q \times m)} \times 100\% \qquad \text{(S3)}$$

where C is phosphate concentration in the desorption solution (mg/L); V is the volume of the desorption solution (L); q is the amount of phosphate adsorbed on the adsorbent beads before desorption (mg/g); and m is the mass of adsorbent beads (g).

Modeling of adsorption kinetics and isotherms

The adsorption kinetics data were fitted with the non-linear pseudo-first-order model (eq. (S4)), non-linear pseudo-second-order model (eq. (S5)), non-linear Elovich model (eq. (S6)), and intraparticle diffusion model (eq. (S7)), and the equations were presented as follows.[1]

Non-linear pseudo-first-order:

$$q_t = q_e(1 - e^{-k_1 t}) \qquad \text{(S4)}$$

Non-linear pseudo-second-order:

$$q_{\mathrm{t}} = \frac{k_2 q_{\mathrm{e}}{}^2 t}{1 + k_2 q_{\mathrm{e}} t} \tag{S5}$$

where q_e (mg-P/g) and q_t (mg-P/g) are the amount of phosphate adsorbed onto the adsorbent at an equilibrium concentration (C_e, mg/L) and a predetermined time (t, min), respectively. k_1 (1/min) and k_2 (g/mg/min) are the rate constants for the pseudo-first-order model and pseudo-second-order model, respectively.

Non-linear Elovich equation:

$$q_t = \left(\frac{1}{\beta}\right) \ln(1 + \alpha\beta t) \tag{S6}$$

where α is regarded as the initial rate (mg g^{-1} min^{-1}), and the β is adsorption constant (g mg^{-1}).

Intra-particle diffusion model:

$$q_{\mathrm{t}} = k_{id} t^{0.5} \tag{S7}$$

where k_{id} (mg/g/$\mathrm{min}^{0.5}$) is the intra-particle diffusion rate constant.

The adsorption isotherms data were fitted by the nonlinear Langmuir model (eq. (S8)) and Freundlich model (eq. (S9)) as follows.[1, 2]

$$q_{\mathrm{e}} = \frac{q_{\mathrm{m}} k_L C_{\mathrm{e}}}{1 + k_L C_{\mathrm{e}}} \tag{S8}$$

$$q_{\mathrm{e}} = k_F C_e{}^{1/n} \tag{S9}$$

where q_e (mg P/g) and q_m (mg P/g) denote the adsorption capacity at equilibrium and predicted maximum adsorption capacity. C_e (mg/L) is the equilibrium phosphate concentration; k_L (L/mg) is the Langmuir adsorption constant; k_F ((mg/g)(L/mg)$^{1/\mathrm{n}}$) and n represent the Freundlich adsorption constant and heterogeneity factor, respectively.

The calculation of distribution coefficient K_d (L/g) was defined as the ratio of adsorbed phosphate to the dissolved phosphate remaining in the solution, which was calculated as follows.[3]

$$K_d = \frac{V \times (C_0 - C_e)}{m \times C_e} \qquad \text{(S10)}$$

where C_o (mg/L) and C_e (mg/L) are phosphate concentrations in the aqueous solutions at the initial time and equilibrium time; V is the volume of the aqueous solution (L); and m is the mass of the beads (g).

Determination of column adsorption performance

The total amount of phosphorus (P) adsorbed onto the adsorbent beads (q_{total}, mg) and the equilibrium adsorption capacity (q_e, mg P/g) were calculated by the following eqs. (S11) and (S12).[4]

$$q_{total} = \frac{Q}{1000} \int_{t=0}^{t=T_{total}} (C_o - C_t)\,dt \qquad \text{(S11)}$$

$$q_e = \frac{q_{total}}{m} \qquad \text{(S12)}$$

where Q (mL/min) is the feed flow rate; C_o (mg/L) and C_t (mg/L) represent the influent and effluent P concentration at the initial stage and t time caused by adsorption. T_{total} (min) is the total time when the column achieves the exhaustion point (C_t/C_0=90%); m (g) is the mass of adsorbent beads packed in the column.

Modeling of column adsorption for breakthrough curves

The fixed-bed column adsorption data were fitted by the Thomas model (eq. (S13)) to predict the breakthrough curves.[1, 2, 4]

$$\ln\left(\frac{C_o}{C_t}-1\right)=k_{Th}q_o\frac{m}{Q}-k_{Th}C_ot \qquad \text{(S13)}$$

where Q (mL/min) is the feed flow rate; C_o (mg/L) is the influent phosphate concentration; C_t (mg/L) is the effluent phosphate concentration at time t (min); k_{Th} (mL/min/mg) is the Thomas rate constant; q_o (mg P/g) is the equilibrium absorption capacity; m (g) is the mass of adsorbent in the column.

Determination of the value of pH at point of zero charge (pH_{pzc})

The pH at point of zero charge (pH_{pzc}) for HZO-PVA and TETA@HZO-PVA was determined by the pH drift method.[5] Specifically, 20 mg of HZO-PVA or TETA@HZO-PVA was added into 80 mL of 0.1 M NaCl solution at desired pH values (2-12). The initial pH (pH_i) of the aqueous solution was adjusted by HCl or NaOH solution (1 M). The final pH (pH_f) was recorded after continuous stirring at 35 ^oC for 24 h. Then the pH_{PZC} is the point where the curve of ΔpH (= pH_f - pH_i) versus pH_i crosses the line equal to zero.

Table S1. Kinetic and isotherm parameters for phosphate sequestration.

Type	Parameter	HZO-PVA	TETA@HZO-PVA
Pseudo-first-order model	q_e (mg/g)	8.80	23.47
	k_1 (min^{-1})	0.006	0.009
	R^2	0.962	0.958
Pseudo-second-order model	q_e (mg/g)	9.74	25.54
	k_2 (g/mg/min)	8.185×10^{-4}	4.867×10^{-4}
	R^2	0.993	0.992
Elovich model	α (mg g^{-1} min^{-1})	0.176	0.963
	β (g mg^{-1})	0.550	0.236
	R^2	0.979	0.958
Langmuir model	q_m (mg/g)	31.23	39.87
	k_L (L/mg)	0.058	0.430
	R^2	0.987	0.956
Freundlich model	k_F ((mg/g)$(\text{L/mg})^{1/\text{n}}$)	3.645	16.595
	n	2.047	4.167
	R^2	0.989	0.980

Table S2. Intraparticle diffusion model parameters for phosphate sequestration.

Step	Parameter	HZO-PVA	TETA@HZO-PVA
Step 1	k_{1d} (mg/g/min$^{0.5}$)	0.448	1.501
	R^2	0.977	0.986
Step 2	k_{2d} (mg/g/min$^{0.5}$)	0.113	0.258
	R^2	0.957	0.948

Table S3 Fitting parameters for O 1s and Zr 3d spectra of virgin and P-loaded HZO-PVA.

Samples	Species	Binding energy (eV)	FWHM (eV)	Aera (cps eV)	Percentage (%)
HZO-PVA	C-O	532.53	1.68	50145.79	54.0
	-OH	530.26	1.68	19422.96	20.9
	O^{2-}	531.39	1.68	23220.87	25.0
	Zr 3d5/2	182.39	1.32	24033.73	60.0
	Zr 3d3/2	184.77	1.32	16026.68	40.0
P-loaded HZO-PVA	C-O	532.60	1.60	51540.27	52.9
	-OH	530.39	1.60	17218.51	17.7
	O^{2-}	531.48	1.60	28660.01	29.4
	Zr 3d5/2	182.60	1.31	22530.13	59.8
	Zr 3d3/2	184.98	1.31	15175.82	40.2

Table S4 Fitting parameters for O 1s, N 1s and Zr 3d spectra of TETA@HZO-PVA before and after phosphate adsorption at different pH conditions.

Samples	Species	Binding energy (eV)	FWHM (eV)	Aera (cps eV)	Percentage (%)
TETA@HZO-PVA	$-NH_2$, -NH-	399.47	1.64	7932.54	65.9
	$-NH_3^+$, $-NH_2^+$	401.94	1.64	4102.30	34.1
	C-O	532.45	1.70	53250.56	67.7
	O^{2-}	531.38	1.70	13385.06	17.0
	-OH	530.20	1.70	11985.58	15.2
	Zr 3d5/2	182.27	1.36	16426.44	60.5
	Zr 3d3/2	184.65	1.36	10718.57	39.5
P-loaded TETA@HZO-PVA at pH 2	$-NH_2$, -NH-	399.52	1.58	5445.04	46.3
	$-NH_3^+$, $-NH_2^+$	401.97	1.58	6308.25	53.7
	C-O	532.60	1.70	69128.38	65.9
	O^{2-}	531.97	1.70	26626.75	25.4
	-OH	530.60	1.70	9153.73	8.7
	Zr 3d5/2	182.67	1.42	10470.41	58.2
	Zr 3d3/2	185.05	1.42	7525.38	41.8
P-loaded TETA@HZO-PVA at pH 8	$-NH_2$, -NH-	399.58	1.72	5144.14	60.6
	$-NH_3^+$, $-NH_2^+$	401.92	1.72	3344.58	39.4
	C-O	532.59	1.66	76511.38	69.3
	O^{2-}	531.58	1.66	21977.44	19.9
	-OH	530.42	1.66	11907.13	10.8
	Zr 3d5/2	182.41	1.41	11460.15	59.7
	Zr 3d3/2	184.79	1.41	7734.13	40.3

Table S5. Column tests conditions and results.

Sample	pH	m (g)	Q (mL/min)	C_o (mg/L)	q_{total} (mg P)	q_e (mg P/g)	Thomas model		
							k_{Th} (mL/(min·mg))	q_o (mg P/g)	R^2
Synthetic solution	5.8	3	5	3.08	83.67	27.89	0.185	28.13	0.984
Real wastewater	7.7	3	5	3.08	60.93	20.13	0.189	20.15	0.961

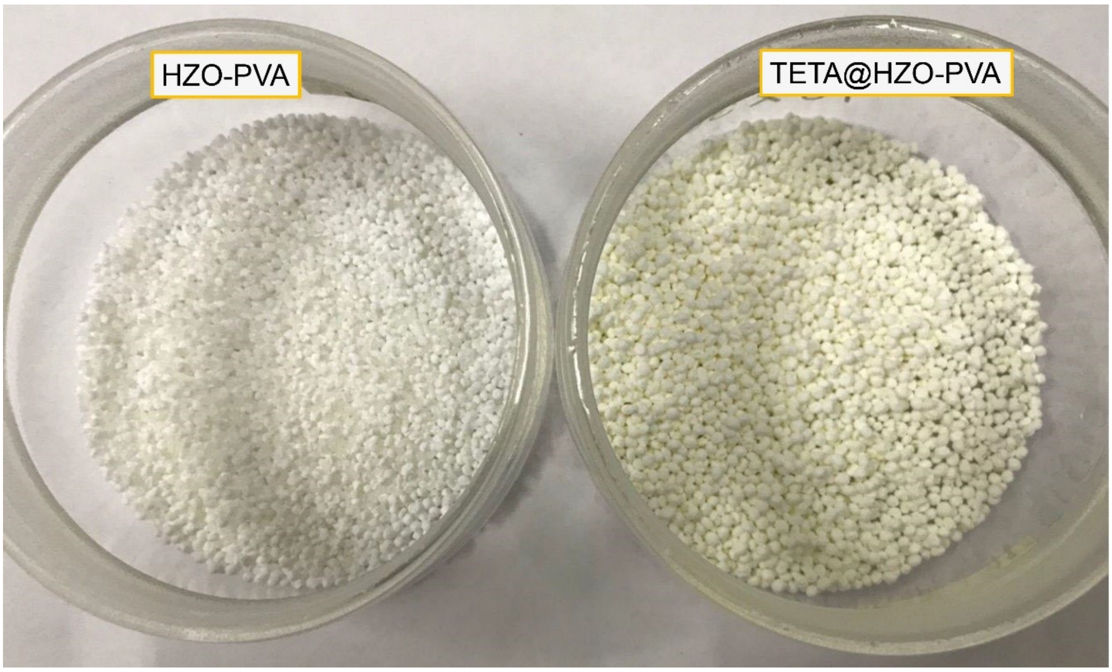

Fig. S1 Photographs of the freeze-dried HZO-PVA and TETA@HZO-PVA composite beads.

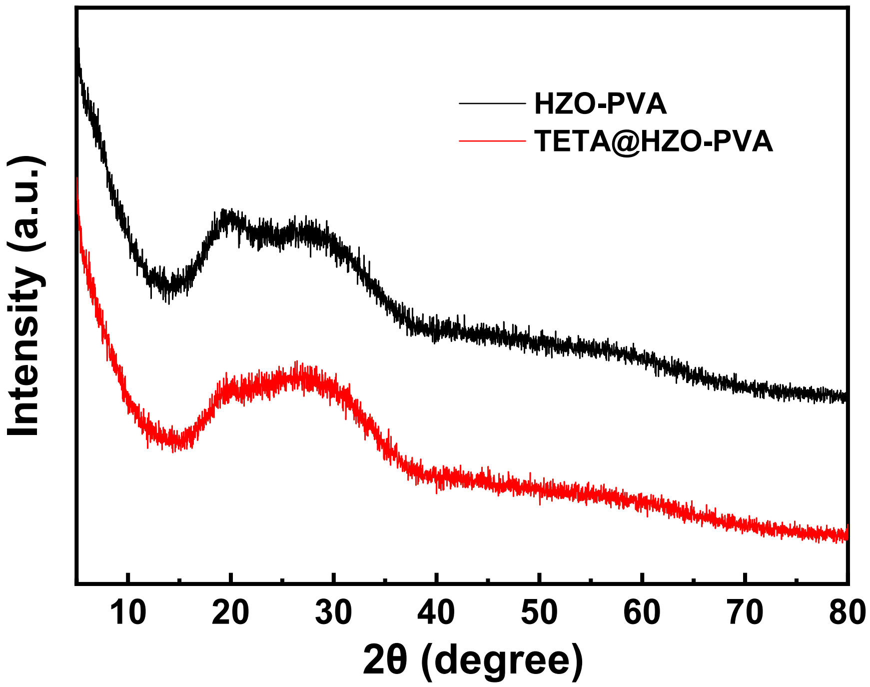

Fig. S2 XRD patterns of HZO-PVA and TETA@HZO-PVA.

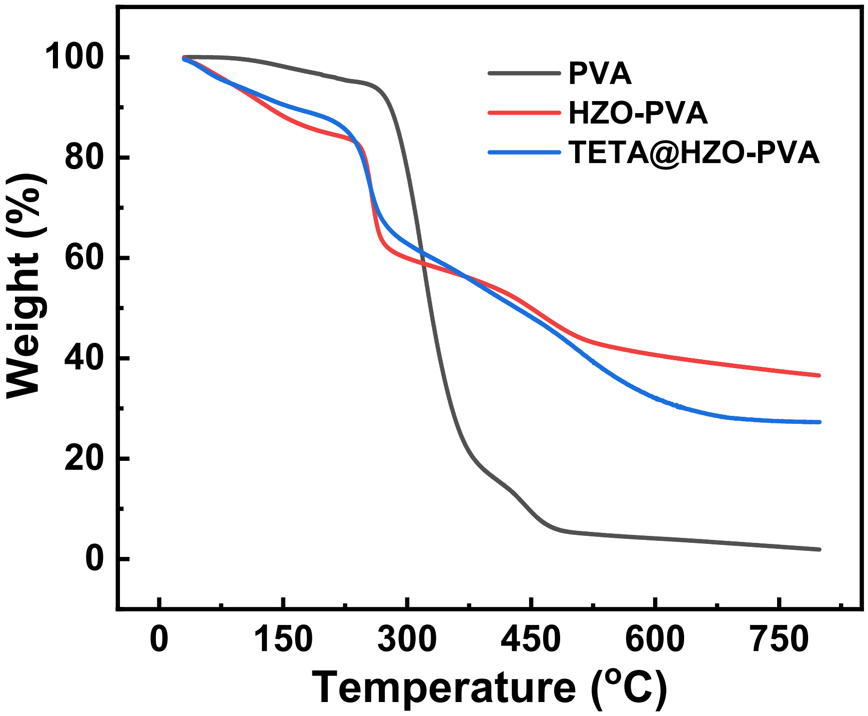

Fig. S3 TGA curves of neat PVA, HZO-PVA and TETA@HZO-PVA.

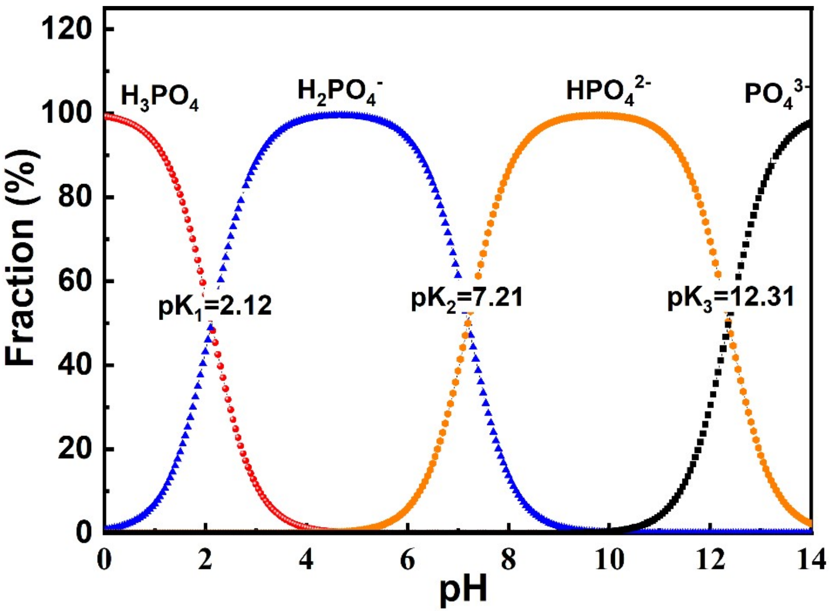

Fig. S4 Distribution of phosphate species as a function of pH.

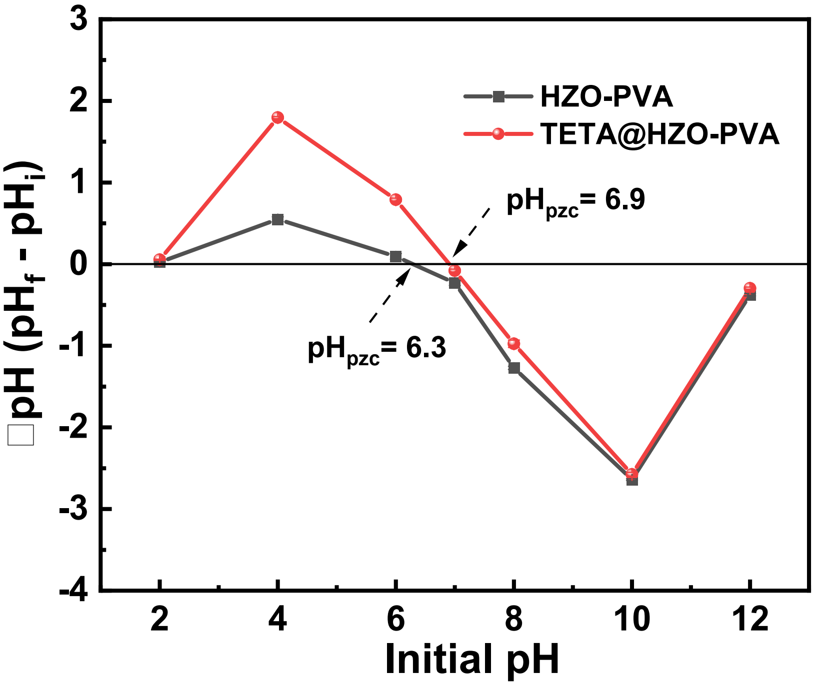

Fig. S5 The pH at point of zero charge (pH$_{pzc}$) for HZO-PVA and TETA@HZO-PVA.

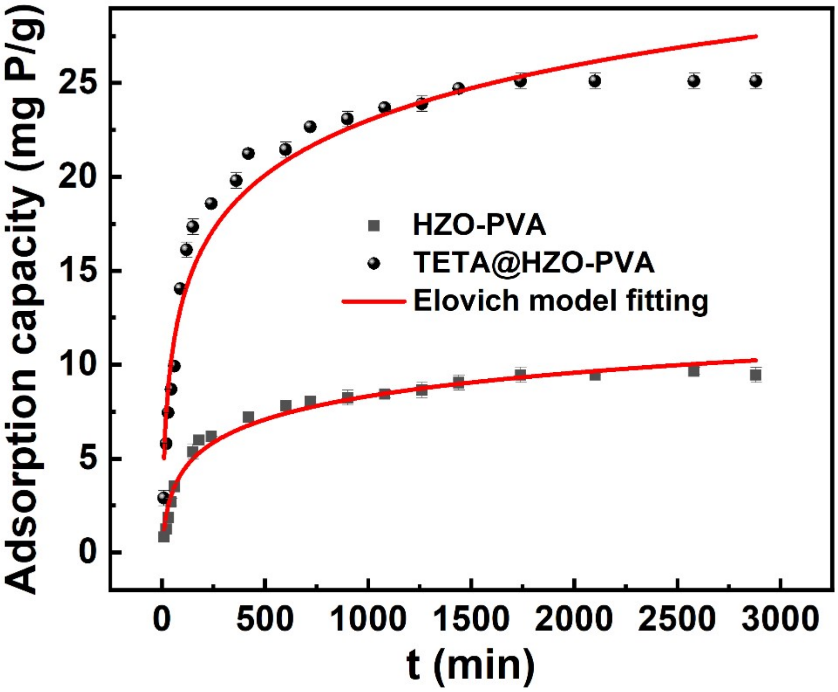

Fig. S6 Phosphate adsorption kinetics onto HZO-PVA and TETA@HZO-PVA with Elovich model fitting.

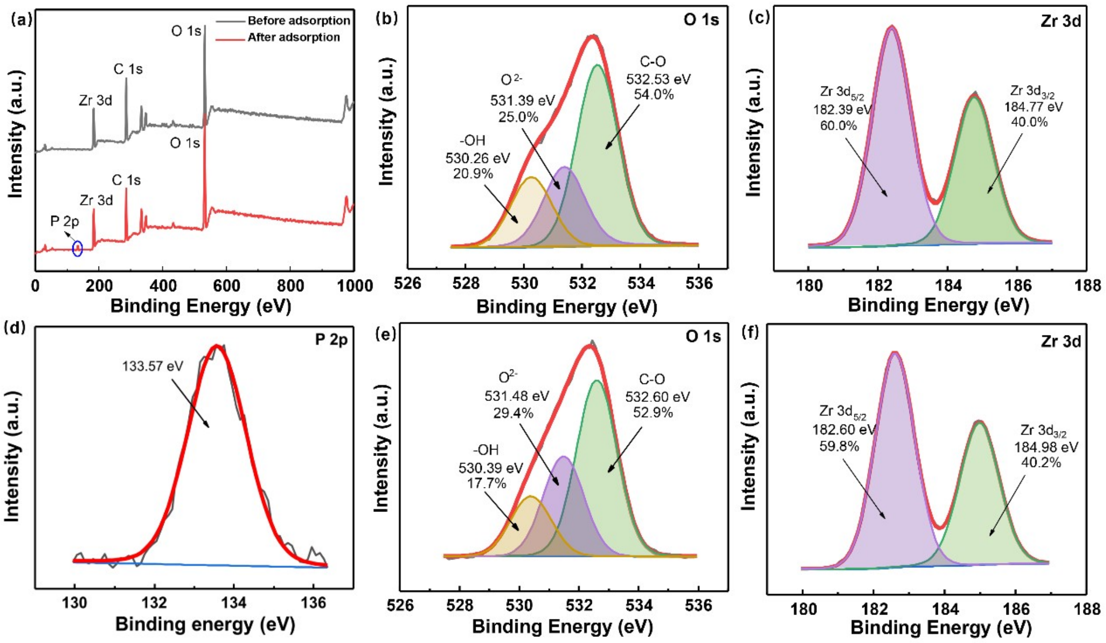

Fig. S7 XPS analysis of HZO-PVA before and after phosphate adsorption: (a) wide-scan spectrum; (b) O1s before adsorption; (c) Zr 3d before adsorption; (d) P 2p; (e) O 1s after adsorption; (f) Zr 3d after adsorption.

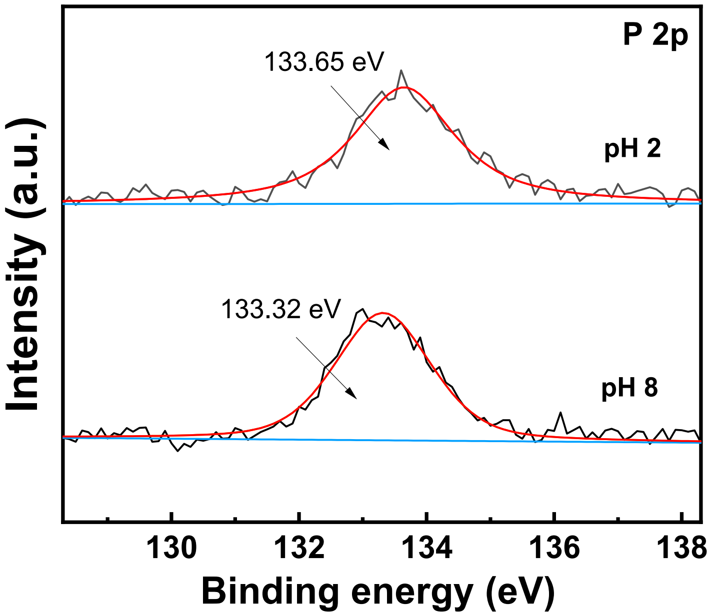

Fig. S8 P 2p XPS spectra of TETA@HZO-PVA after phosphate adsorption at pH 2 and 8.

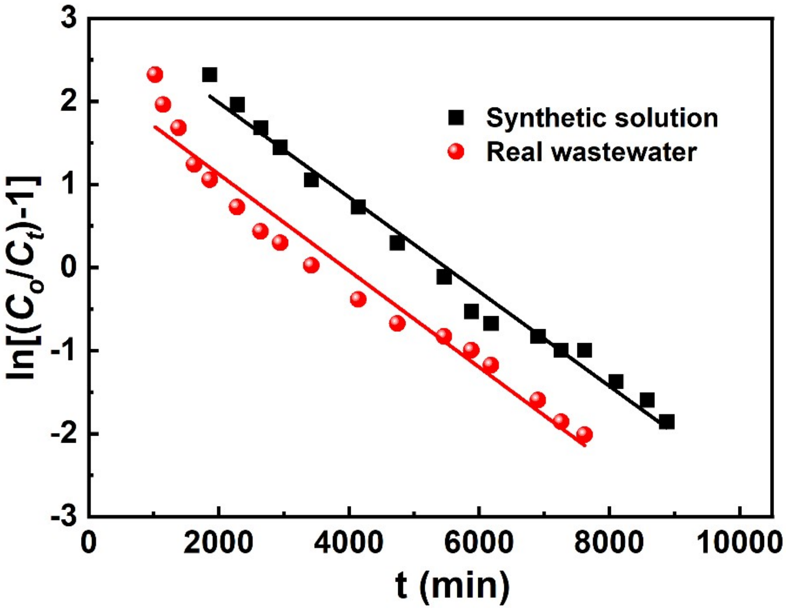

Fig. S9. Plots of linear regressions on Thomas model.

References

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