Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts.

A novel Ca/Mn modified biochar recycles P from solution: mechanisms and phosphate efficiency

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1. **Materials and methods**

1.1 Effects of coexisting anions strength

Analysis of different coexisting ions strength on phosphate (P) adsorption, 0.1, 0.01 M and 0.001 M $NaNO_3$ were applied to prepare different initial P concentrations (0-75 mg·L^{-1}) to explore the effect of anions on P removal. The adsorbents (each with 0.08 g) were added into the phosphate solutions before shaken at 120 rmp for 24 h.

1.2 Adsorption thermodynamics

The adsorption was performed at the temperature of 15, 25 °C and 35 °C respectively for thermodynamic analysis. The sorption process is same as the isothermal adsorption experiment (adding 0.1 g biochar into 40 mL brown glass bottles that contain 20 mL various initial phosphate concentrations (1-75 mgP·L^{-1}). The equilibrium phosphate concentrations were determined via ultraviolet spectrophotometer.

1.3 Stability analysis of CMBC

0.2 g of the modified biochar (CM_1BC) was added to 20.0 mL solution containing 20.0 mL DI water solution set at various pH values (pH:3, 4, 5, 6, 7, and 8) in brown glass bottles and shaken at 120 rpm (end to end) at an ambient temperature for 24 h. Then, the Subsequently, the suspension was filtered and measured. The phosphate desorption ratio was calculated following Eq.(10):

$$\text{dissolved amounts} = \frac{Ce \times V}{M} \times 1000 \qquad (10)$$

where C_e (mg/L) is the equilibrium concentration of Mn/Ca in the solution. V (mL) is the volume of water, and M (g) is the mass of the CMBC.

2. Results and discussion

2.1. Effect of coexisting ionic strength

Coexisting ions in natural, agricultural or industrial wastewaters may affect the P adsorption capacity due to the coulombic forces or competing adsorption sites. Thus, it is imperative to explore effects of the coexisting ionic strength on P adsorption. As shown in Fig. S8, the initial P and NO_3^- concentrations are ranged between 0 mg·L^{-1} to 75 mg·L^{-1} and 0.001 to 0.1 M, respectively, while mass of the modified biochars (CBC, MBC, CM_1BC and CM_2BC) added in the solutions are 4 g·L^{-1}, It is observed that 0.001 and 0.01 M NO_3^- have little effect on P adsorption on the four modified adsorbents. In the presence of 0.1 M NO_3^-, there is a relatively small drop in the P adsorption capacity of the CBC and MBC in this study, which agree with previous observations where La modified vermiculites materials and calcium-activated biochar were used on P adsorption (Huang et al., 2014; Liu et al., 2019). However, the P adsorption capacity of the CM_1BC and CM_2BC decline, but these adsorbents still show a remarkable P sorption capacity when the concentration of NO_3^- reached 0.1 M.

2.2 Thermodynamic study

Fig.S9 shows, the P adsorption capacity increased with the increase of the sorption temperatures from 15°C to 35 °C, which imply that higher temperature has a positive effect on P adsorption capacity.

To further evaluate the stability and feasibility of the phosphate adsorption on the adsorbents, three thermodynamic parameters such as Gibbs free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) were calculated by the Eq. (10) and (11):

$$\Delta G^0 = -RTlnK_L \quad (10)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (11)$$

where R is the universal gas constant (8.314 J·mol^{-1}·K^{-1}), T is the absolute temperature (K), and K_L (L·mol^{-1}) represents the Langmuir adsorption characteristic constant.

The corresponding thermodynamic parameters are shown in Table S4. The CM_1BC for an example, the change in negative values of the ΔG^0 reveal that the phosphate adsorption on CBC, MBC, CM_1BC and CM_2BC were a spontaneous process (Table S4). When the temperature is raised from 15 to 35 °C, there is a drop of ΔG^0 from -23.57 kJ·mol^{-1} to -28.40 kJ·mol^{-1}, which showed that the spontaneity increases with the increase of temperatures. The positive value of ΔH^0 (56.61 kJ·mol-^{1}) indicates that the phosphate adsorption on the CM_1BC sample was an endothermic process, and the adsorbents would possess higher phosphate adsorption with the increasing temperature (Ajmal et al., 2020). Moreover, the higher temperature may increase the diffusion of phosphate ions in solution and enhance the probability of phosphate collision between the active sites and the phosphate ions (Liu et al., 2019). Additionally, the positive value of ΔS^0 (0.241 $kJ\cdot mol^{-1}\cdot K^{-1}$) elucidates that the randomness of adsorbent-liquid interface increased during the phosphate sorption process with the increase of temperature. The thermodynamic parameters analysis of other adsorbents such as CBC, MBC and CM_2BC agree with CM_1BC (Table S4).

2.3 Stability analysis of CMBC

In order to investigate the stability and potential risk of the adsorbed material, the amount of Ca and Mn released from CMBC was measured in different pH solutions. It can be seen in Fig S10, at low pH values (3.0-5.0) the amount of Ca, Mn released was found to be in the range of 8.6 - 14.4 $\mu g\cdot g^{-1}$ and 1.4 to 3.3 $\mu g\cdot g^{-1}$. Under acidic conditions, Ca, Mn were more readily released, but the overall dissolved amounts were relatively low (Ca: < 15 $\mu g\cdot g^{-1}$; Mn <4 $\mu g\cdot g^{-1}$). The dissolution of Ca and Mn is further reduced as pH > 5.0 (Ca: < 7 $\mu g\cdot g^{-1}$; Mn <1 $\mu g\cdot g^{-1}$). These results indicated that CMBC possesses good stability and relatively low risk.

References：

Ajmal, Z., Muhmood, A., Dong, R., et al.,2020 Probing the efficiency of magnetically modified biomass-derived biochar for effective phosphate removal[J]. J. Environ. Manage. 253, 109730.

Huang, W.Y., Li, D., Liu, Z.Q., et al., 2014. Kinetics, isotherm, thermodynamic, and adsorption mechanism studies of $La(OH)_3$-modified exfoliated vermiculites as highly efficient phosphate adsorbents[J]. Chem. Eng. J. 236, 191-201.

Liu, X.N., Shen, F., Qi, X.H., 2019. Adsorption recovery of phosphate from aqueous solution by CaO-biochar composites prepared from eggshell and rice straw[J]. Sci. Total Environ. 666, 694-702.

Table S1 The basic physicochemical characteristics of soil

Available phosphorus（$mg \cdot kg^{-1}$）	Available potassium（$mg \cdot kg^{-1}$）	Total nitrogen（%）	Organic matter（%）	pH
10.4	200.0	0.195	3.94	6.25

Table 2 Langmuir, Freundlich and Sips equation parameters of phosphate adsorption onto different biochar

Adsorbents	Langmuir				Freundlich			Sips			
	Q_m (mg·g^{-1})	K_L (L·mg^{-1})	R_L	R^2	1/n	K_F	R^2	Q_m (mg·g^{-1})	Ks (L·g^{-1})	γ	R^2
CBC	9.15	1.38	0.0096	0.988	0.26	4.07	0.88	9.20	1.35	0.97	0.986
MBC	3.19	0.30	0.0430	0.989	0.18	1.43	0.87	3.53	0.22	0.78	0.991
CM_1BC	15.58	1.21	0.0109	0.978	0.16	8.81	0.93	17.23	1.03	0.64	0.984
CM_2BC	20.84	0.68	0.0192	0.988	0.28	8.84	0.92	19.68	0.83	0.95	0.992

Table S3 The maximum phosphate sorption capacities reported in the references via different sorbents

Adsorbents	pH	Qm(mg $P \cdot g^{-1}$)	References
Ca-Mn impregnated biochar	≈6.5	20.8	This study
Mg-modified dealbata biochar	7	9.0	Cui et al., 2016
Fe-activated carbon	6.5	10.8	Kumar et al., 2017
La-modified carbon	-	13.3	Koilraj et al.,2017
Fe-Mn oxide	7	18.4	Du et al.,2017
$Ca(OH)_2$-modified natural zeolite	7 7	8.8	Mitrogiannis et al.,2017
Eggshell biochar	-	32.6	Kose et al.,2011

Table S4 Thermodynamic parameters for phosphate adsorption on different adsorbents

Adsorbents	Temperature(K)	ΔG^0(kJ/mol)	ΔH^0(kJ/mol)	$\triangle S^0$(kJ/(mol·K))
CBC	288.15	-24.05	59.68	0.291
	298.15	-26.96		
	308.15	-29.86		
MBC	288.15	-19.33	56.610	0.264
	298.15	-21.97		
	308.15	-24.60		
CM_1BC	288.15	-23.57	45.90	0.241
	298.15	-25.98		
	308.15	-28.40		
CM_2BC	288.15	-22.55	41.18	0.221
	298.15	-24.76		
	308.15	-26.97		

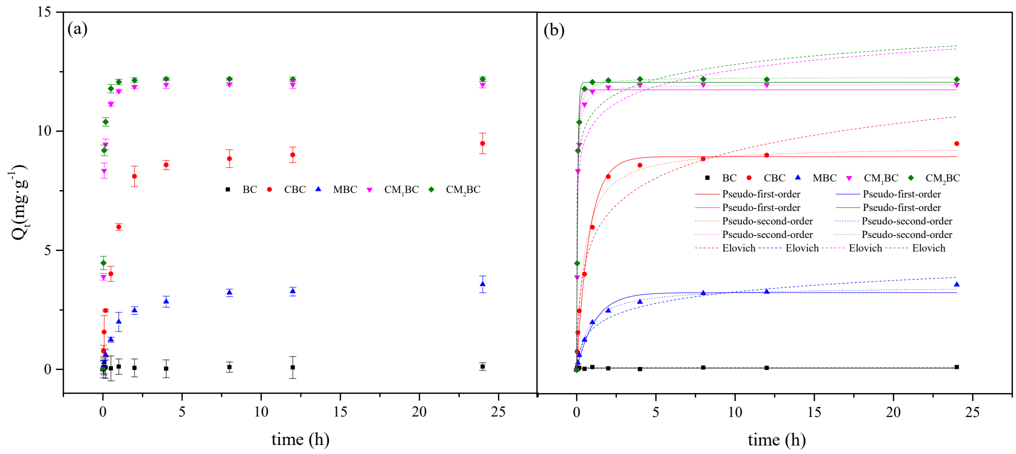

Fig. S1. Adsorption kinetics of phosphate onto pristine biochar and modified adsorbents.

Fig.S2 Effects of different usage of BC/CMBC/P-CMBC on rape seedling growth

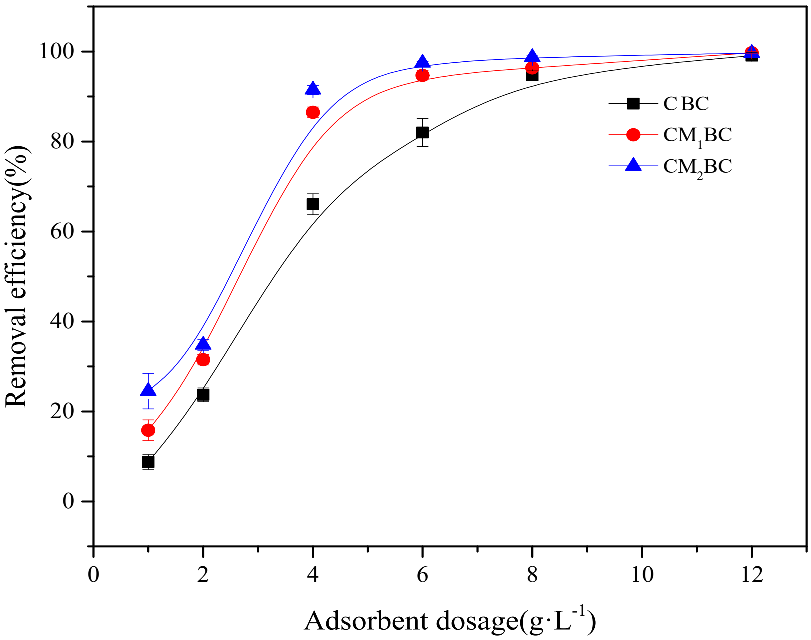

Fig.S3. Effects of adsorbent dosage on phosphate sorption capacity by CBC, CM_1BC, and CM_2BC

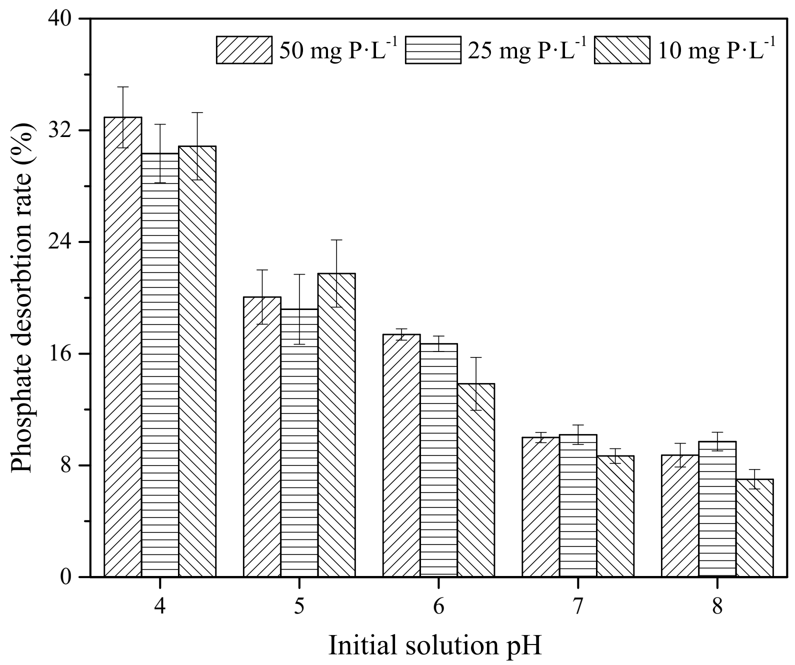

Fig. S4. Phosphate desorption by meas of DI water in various pH

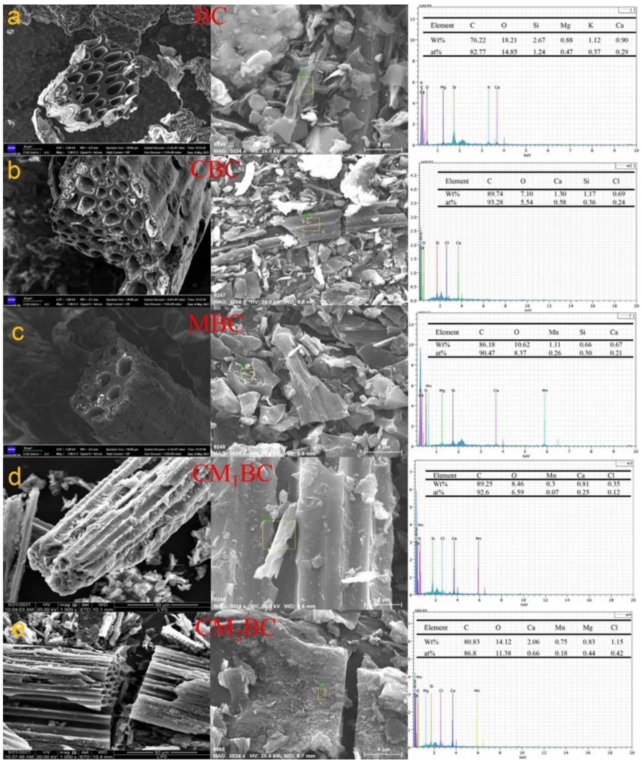

Fig.S5.SEM images and EDS spectra of (a) BC, (b) CBC, (c) MBC,(d) CM_1BC, (e) CM_2BC

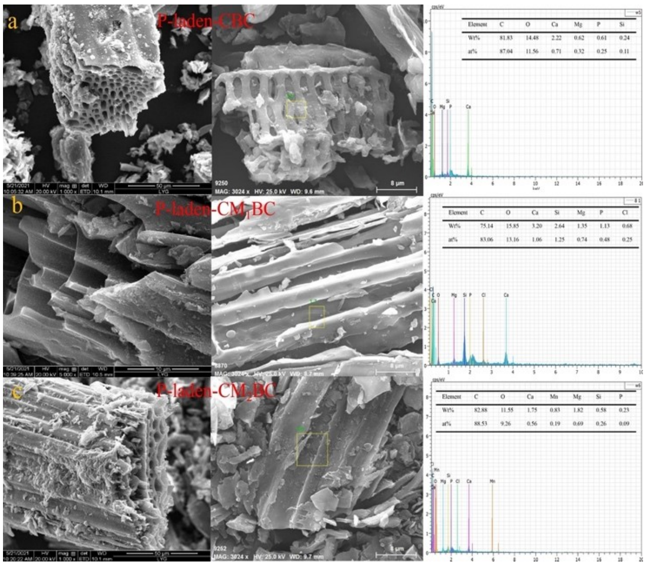

Fig.S6. SEM images and EDS spectra of (a) P-laden-CBC, (b) P-laden-CM_1BC, (c) P-laden- CM_2BC

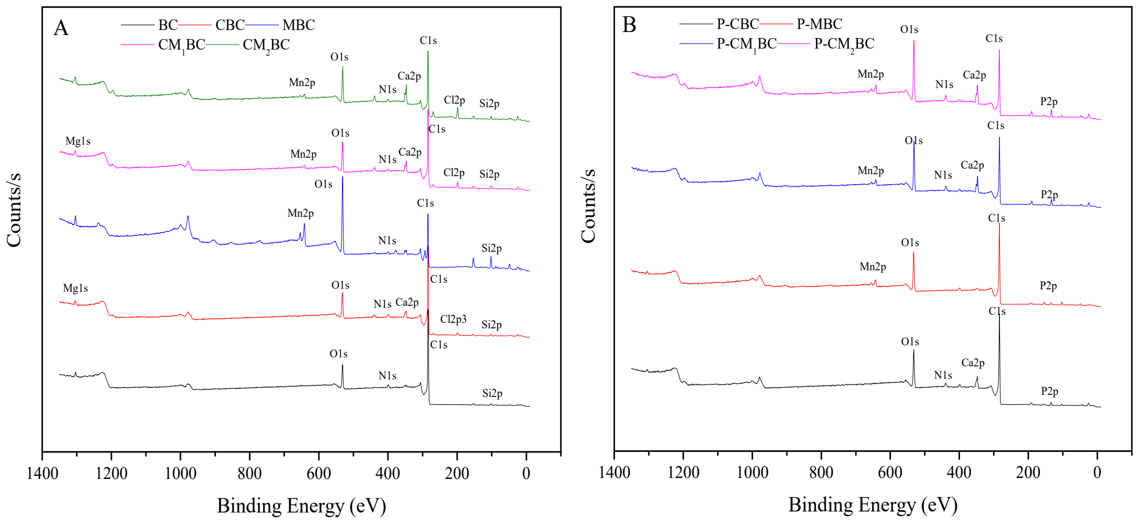

Fig. S7. Pristine biochar and modified adsorbents before or after phosphate sorption: (A)BC, CBC, MBC, CM_1BC, and CM_2BC; (B) P-CBC, P-MBC, P-CM_1BC, and P-CM_2BC

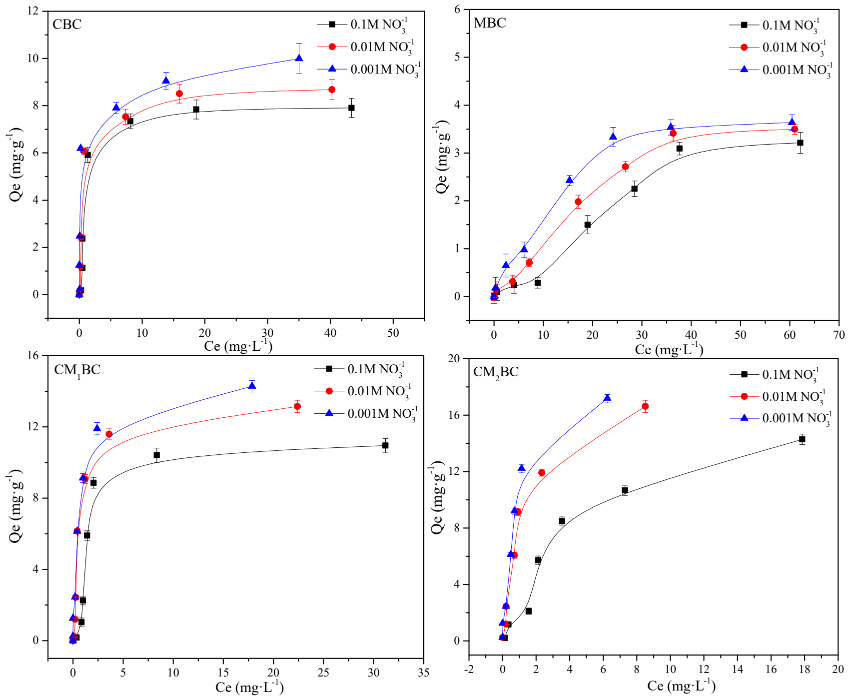

Fig. S8. Effect of coexisting ionic strength on the removal of phosphate by modified adsorbents

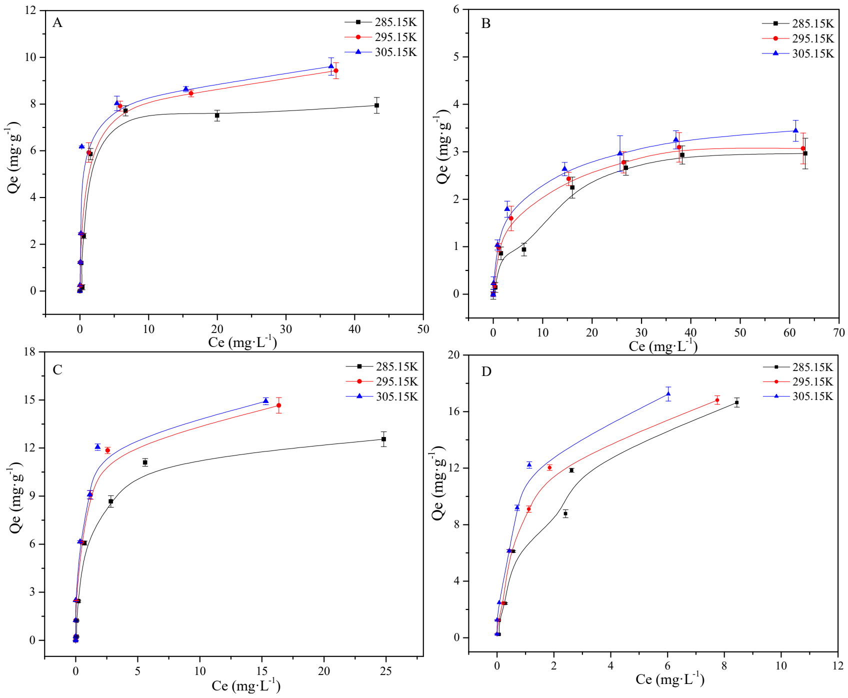

Fig. S9. Effect of various temperatures on the removal of phosphate by different adsorbents:(A)CBC; (B)MBC; (C)CM_1BC; (D)CM_2BC

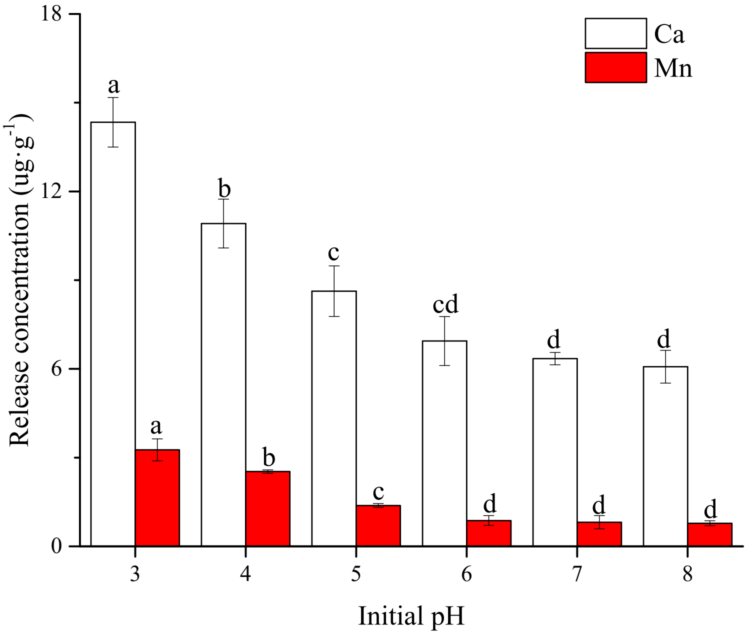

Fig. S10. The concentrations of Ca and Mn in various pH