Supporting Information for

Adsorption removal Mn^{2+} and NH_4^+-N from electrolytic manganese metal wastewater by modified phosphate ore flotation tailings

Yuhao Wu[a], Jiancheng Shu[a*], Wenxing Cao[a], Zihan Li[a], Bing Li[b], Zhonghui Xu[a], Hongliang Chen[a,c], Mengjun Chen[a], Zongyu Deng[d]

a. *Key Laboratory of Solid Waste Treatment and Resource Recycle (SWUST), Ministry of Education, Southwest University of Science and Technology, 59 Qinglong Road, Mianyang, 621010, China*

b. *School of Chemistry and Chemical Engineering, Yangtze Normal University, Chongqing, 408100, China*

c. *College of Chemistry and Chemical Engineering, Anshun University, Anshun, Guizhou, 561000, PR China*

d. Zunyi manganese day magnetic industry group co.,Ltd, Zunyi, Guizhou, 563000, China

Figure list

Table list

Calculation formula

The calculation formula for the adsorption capacity at equilibrium (q_e, mg/g) and the adsorption capacity at different time "t" (q_t, mg/g) are as follows:

$$q_e = \frac{(C_0 - C_e) \times V}{m} \quad (1)$$

$$q_t = \frac{(C_0 - C_t \times V)}{m} \quad (2)$$

Where C_o, C_e and C_t are the initial, equilibrium concentration (mg/L) of NH_4^+-N and the concentration of NH_4^+-N at different time "t", respectively. V is the volume of the EMMW (L), and m is the mass of the MPOFTs (g).

Analysis methods

The concentrations of Mn^{2+} and other heavy metals were determined by Atomic Absorption Spectrophotometry (AAS) (HITACHI 180/80, Japan) in flame. The concentration of NH_4^+-N was determined via Nessler's Reagent spectrophotometry. The pH of the solution was measured by using ultra-microvolume pH electrodes (PHS-3C, Shanghai, China). The precipitates composition and properties were analyzed via X-ray diffraction instrument (XRD; JapanD/maxIIIA), Scanning Electron Microscope (SEM; Slgma 300) and X-ray fluorescence (XRF; PANalytical B.V., Axios; Netherlands). The Magna 550II FTIR Spectrometer (Perkin Elmer Frontier) was used to obtain the FT-IR spectra of the sample via the KBr particle method. According to the extraction procedure of solid waste, the toxic leaching method of horizontal vibration was selected (HJ 557-2010)

S1 Equilibrium adsorption isotherms

The equilibrium adsorption isotherm is an important data model that can reflect the surface properties and adsorption behavior of adsorbents. It can be fitted by Langmuir model and Freundlich model and expressed as an equation in linear form.

Langmuir model: $$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (1)$$

Where K_L is the adsorption equilibrium constant (L/ mg), q_m is the maximum monolayer

adsorption capacity, and q_e is the amount adsorbed on a unit mass of the adsorbent (mg/g) when the equilibrium concentration is C_e (mg/L).

Freundlich model:
$$\ln q_e = \frac{\ln C_e}{n} + \ln K_F \quad (2)$$

where K_F ((mg/g) (L/g)^n) and n are Freundlich constants related to sorption capacity and sorption intensity of adsorbents.

Fig.S1a

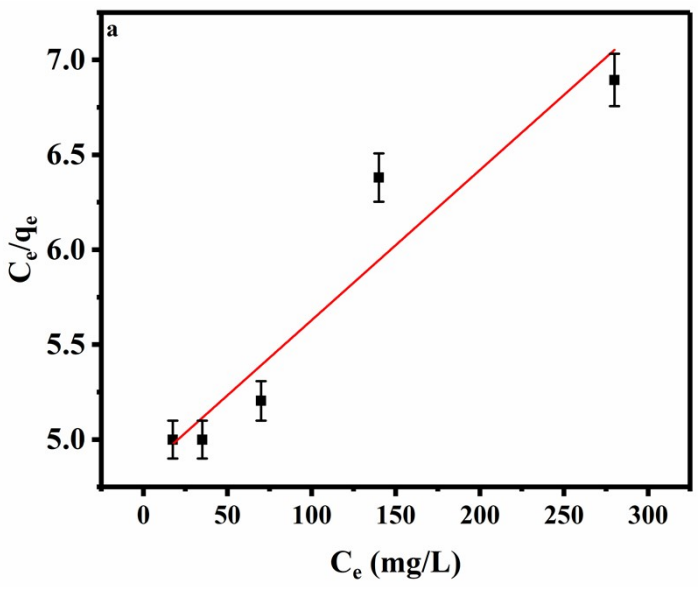
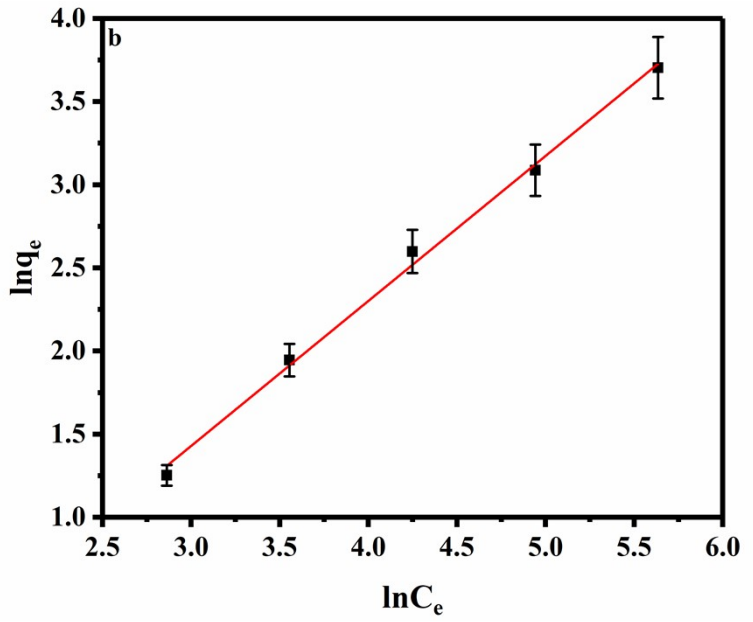


Fig.S1b



S2 Adsorption kinetics

Adsorption kinetics is composed of pseudo-first-order and pseudo-second-order kinetic models. They were analyzed to test the experimental data. These two models can be expressed in a linear form as Eqs. (3) and (4), respectively.

The pseudo-first-order kinetic model: $\ln\ (q_e - q_t) = \ln q_e - K_1 t$ (3)

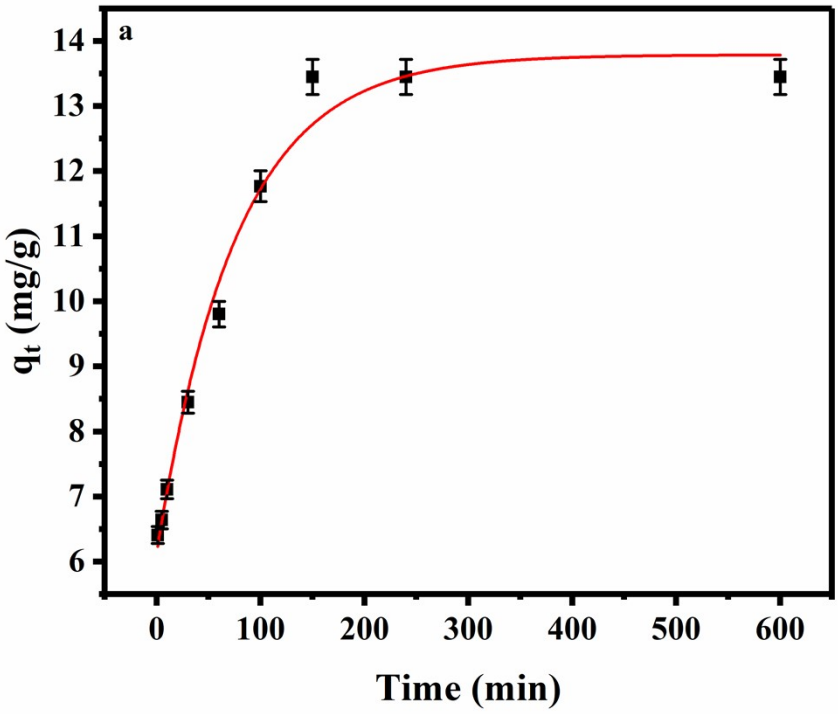
The pseudo-second-order kinetic model: $$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{t}{q_e}$$ (4)

The steps of adsorption process were studied with Weber's intraparticle diffusion model. It can be expressed as Eq.(5).

Weber's intraparticle diffusion model: $q_t = K_i t^{\frac{1}{2}} + C$ (5)

where k_i (mg/g/min$^{1/2}$) is the intraparticle diffusion rate constant and C (mg/g) represents the intercept.

Fig.S2a



1

2

Fig.S2b

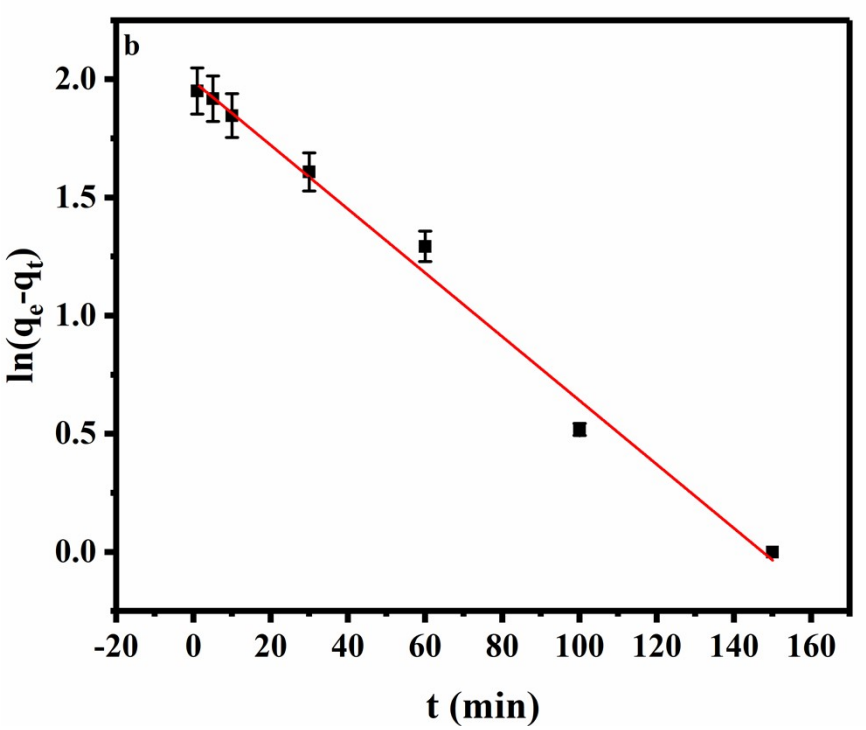


Fig.S2c

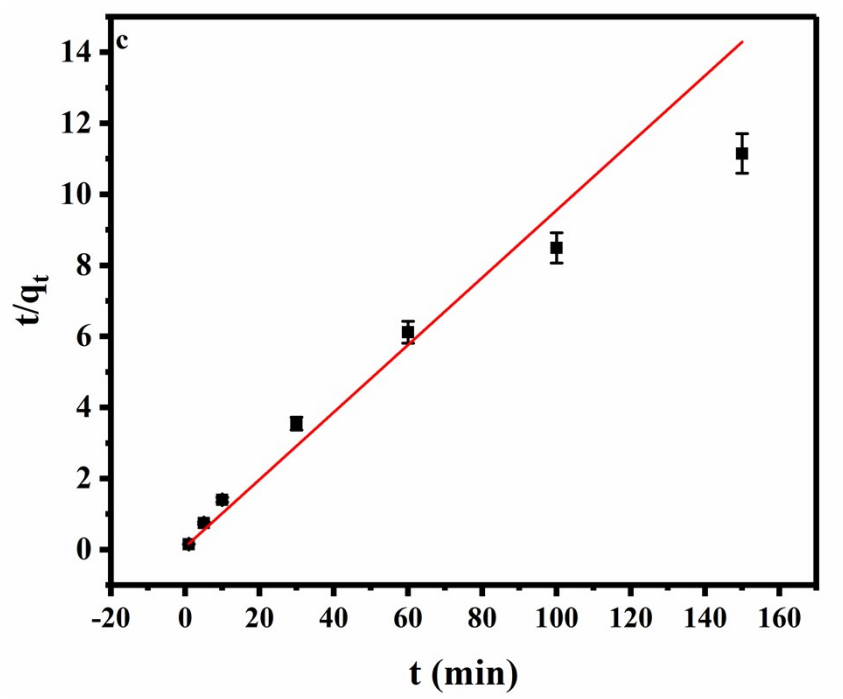
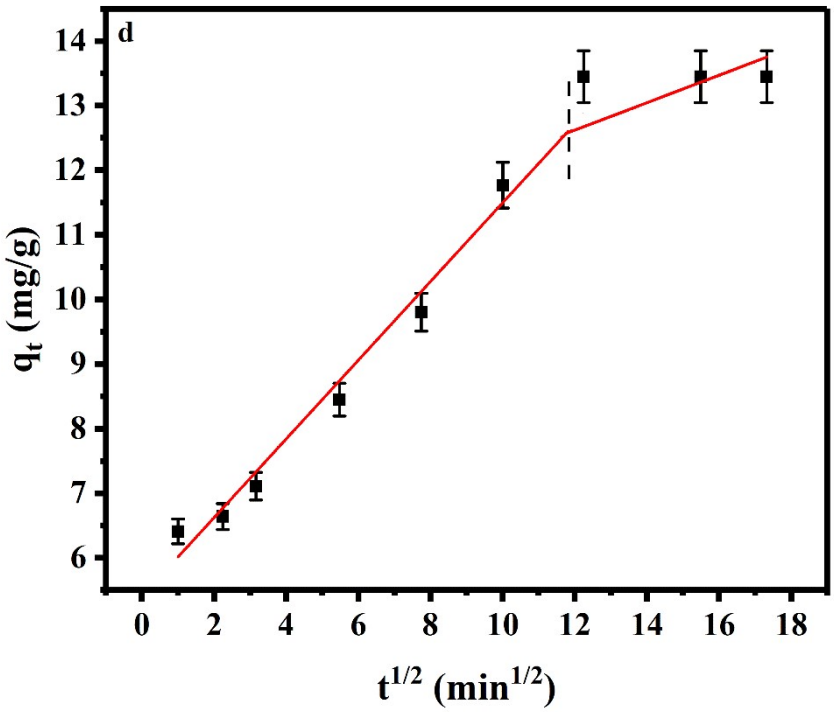


Fig.S2d



S3 Adsorption thermodynamics

Adsorption thermodynamics will explore the enthalpy change($\triangle H^0$) and Gibbs free energy change($\triangle G^0$) generated during the adsorption process. The enthalpy change data will be obtained by fitting the Clausius-clapeyron model. Gibbs free energy change will be derived from the Gibbs equation.

Clausius-clapeyron model: $$\ln C_e = \frac{\Delta H}{RT} + C \quad (6)$$

Gibbs equation: $$\Delta G = -RT\ln K_L \quad (7)$$

Where K_L is the Langmuir equilibrium constant (L/mol); R and T represent the universal gas constant (8.314 J/K/mol) and the system temperature (K), respectively.

Fig.S3

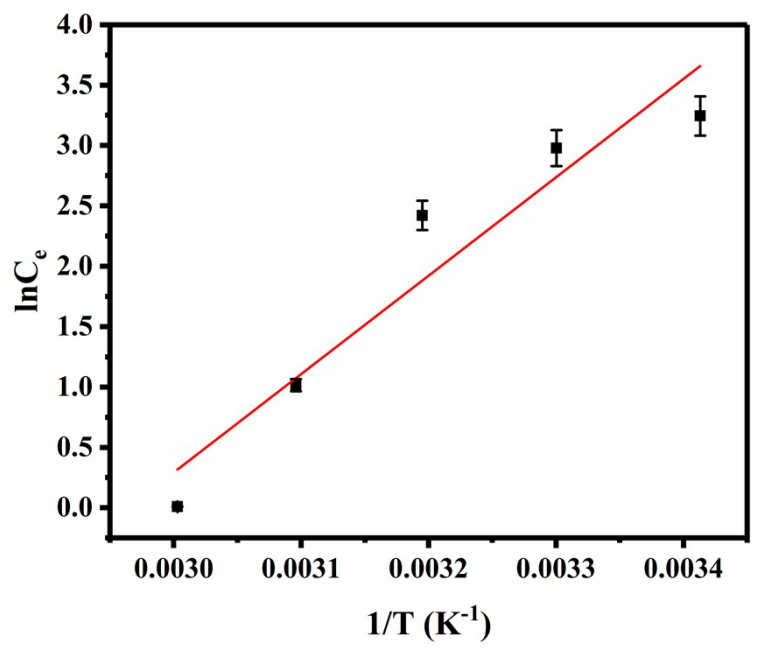


Table S1 Adsorption free energy change

Adsorption free energy change	
T （K）	ΔG（J/mol）
293	-2793.36
303	-2888.70
313	-2984.04
323	-3079.37
333	-3174.71
343	-3270.05

Table S2 XRF analysis of the POFTs and MPOFTs

	Parameter	CaO	MgO	P_2O_5	SO_3	SiO_2	F	Fe_2O_3	Al_2O_3	MnO	K_2O	Na_2O	SrO	TiO_2	ZnO
POFTs	**Percentage (%)**	57.26	16.89	9.78	8.16	3.53	1.70	1.06	0.81	0.29	0.19	0.07	0.05	0.05	0.04
MPOFTs	**Percentage (%)**	64.13	22.14	6.52	0.73	3.15	0.31	1.67	0.89	0.48	0.20	/	0.04	/	0.05

Table S3 Surface areas of the POFTs and MPOFTs

Samples	POFTs	MPOFTs
BET surface area （m^2/g）	2.2956	6.5239
BJH desorption pore volume（cm^3/g）	0.0049524	0.038057

Table S4 ICP analysis of leachates (mg/L) (1#: POFTs, 2#:MPOFTs, 3#: EMMW,4#: MPOFTs after adsorption).

	NH_4^+-N	Mg^{2+}	Mn^{2+}	Ca^{2+}	Zn^{2+}	Sb^{2+}	Co^{2+}
1#	/	22.38	0.03	3.03	/	/	/
2#	/	108.32	/	0.01	/	/	/
3#	70.00	45.00	165.00	9.00	0.06	0.03	0.01
4#	1.73	78.47	0.001	5.85	/	/	/