
NAXOS2018
13-16 June 2018
6th International
Conference
on
Sustainable Solid Waste
Management

NAXOS 2018

6th International Conference on Sustainable Solid Waste Management

Sludge Management

Dynamic adsorption behaviors of Pb^{2+} under complex conditions in biochar fixed-bed system: breakthrough curve characteristics and parameters

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2018.06.15

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1. Introduction

In recent years the metallic lead, lead alloys and lead compounds had been widely applied in storage battery, machine building, shipbuilding, light manufacturing, radiation protection, etc.

Natural water body have been heavily contaminated by lead wastes in the application of lead. Consequently, the treatment and disposal for lead pollution have been the focal and heated point in the field of water environment protection.

These several years, the production of activated sludge was increased with the increasing of population and water consumption in the proceeding of urbanization. Previous investigations have shown that the activated sludge can be used as crude material for adsorption of pollutants through carbonization.

1. Introduction

Position of mine

Pb-Zn mixed ores

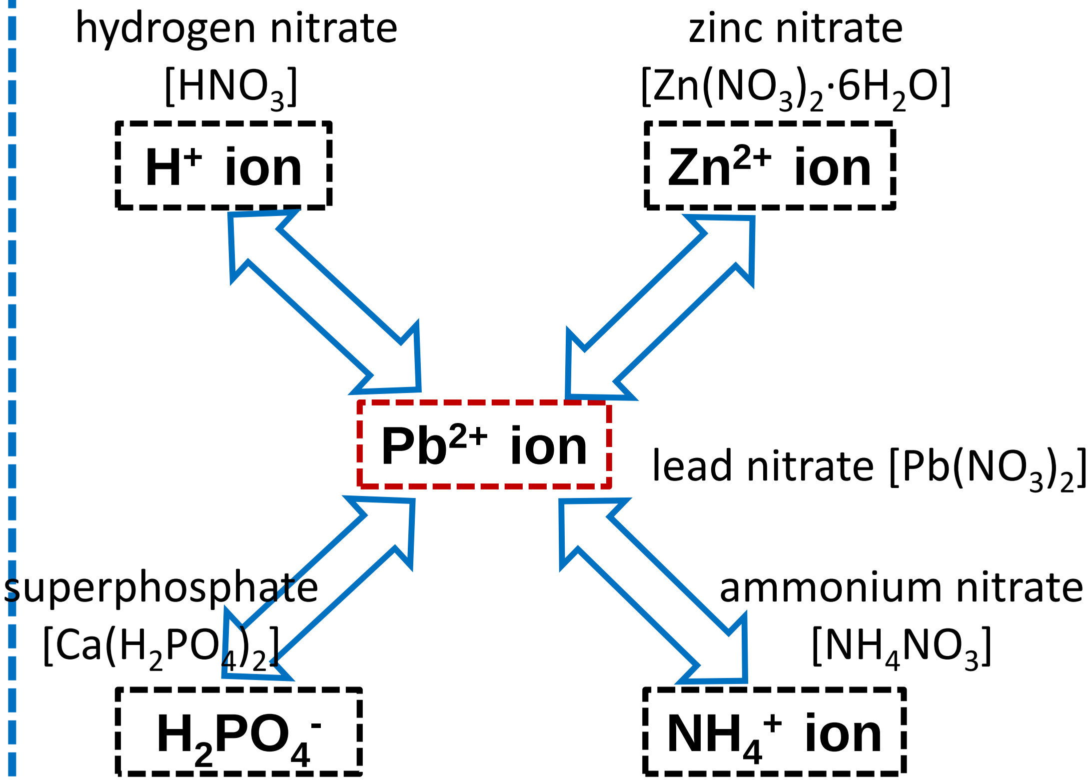
Phosphate fertilizer

In the smelting, processing and treatment procedure of ore, the combined action of **lead** and **zinc** is prerequisite to be taken into account.

Meanwhile, the mining is always located in the remote region in general near to agriculture area. The local natural water body is readily influenced by the mining, processing and transportation procedure of heavy metal.

Based on the requirement of agricultural production, **nitrogen fertilizer** (NH_4NO_3, NH_4HCO_3, etc.) and **phosphate fertilizer** ($Ca(H_2PO_4)_2$, $Ca_3(PO_4)_2$, etc.) were widely applied to the fields. But a majority of fertilizer were not fully utilized and finally leached to local water, which led to serious water pollution.

1. Introduction



The influence of co-existing ions on adsorption of Pb^{2+} ion in fixed-bed system

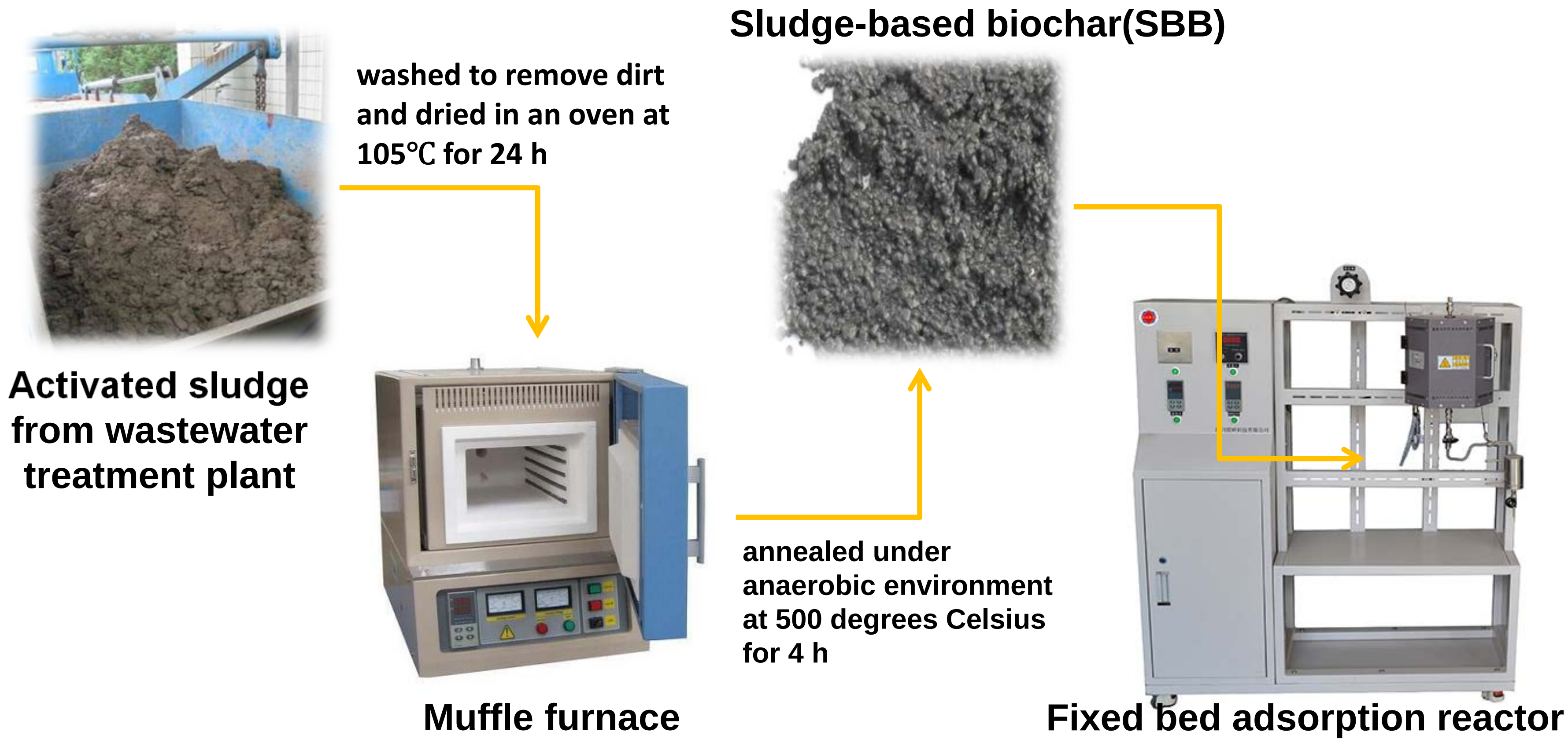
In consideration of all aforementioned situation, in order to ascertain the actual treatment efficiency of target contaminant, and clarify the interrelationship between different contaminants, it is necessary to research the actual removal effect of Pb^{2+} under the complex environment containing **pH**, **zinc**, **ammonia nitrogen** and **phosphorus**.

1. Introduction

Sludge-based biochar(SBB)

In this study, fixed-bed system was constructed by glass columns packed with SBB. The effect of **Zn^{2+}, NH_4^+, $H_2PO_4^-$** and their combined systems on fixed-bed adsorption preference for Pb^{2+} ion were studied. The main objective of this study was to determine the adsorption behaviors of Pb^{2+} in fixed-bed under **complex environment**.

2. Materials and methods



2. Materials and methods

Investigated systems in this research

System	co-existence ions concentration
1)Pb^{2+}	pH=3.0 pH=4.5 pH=6.0
2)Pb^{2+}-Zn^{2+}	0.5 1.0
3)Pb^{2+}-NH_4^+	0.5 1.0
4)Pb^{2+}-$H_2PO_4^-$	0.5 1.0
5)Pb^{2+}-Zn^{2+}-NH_4^+	1.0/1.0
6)Pb^{2+}-Zn^{2+}-$H_2PO_4^-$	1.0/1.0
7)Pb^{2+}-NH_4^+-$H_2PO_4^-$	1.0/1.0
8)Pb^{2+}-Zn^{2+}-NH_4^+-$_2PO_4^-$	1.0/1.0/1.0

(**M_{ad}, mmol**): total mass of Pb^{2+} ion adsorbed by fixed-bed

(**q_d, mmol/L**): dynamic adsorption capacity

(**H, cm**): height of mass transfer zone

(**R, %**): total metal removal rate of fixed-bed

t_b and **t_e** are the time (min) of breakthrough point (C_t/C_0=10%) and exhaustion (saturation) point (C_t/C_0=95%)

Two fixed - bed adsorption models were proposed to simulate the adsorption dynamic processes:

Thomas model

Yoon-Nelson model

3. Results and Discussion

3.1 Breakthrough curve of Pb^{2+} ion adsorption process under different pH

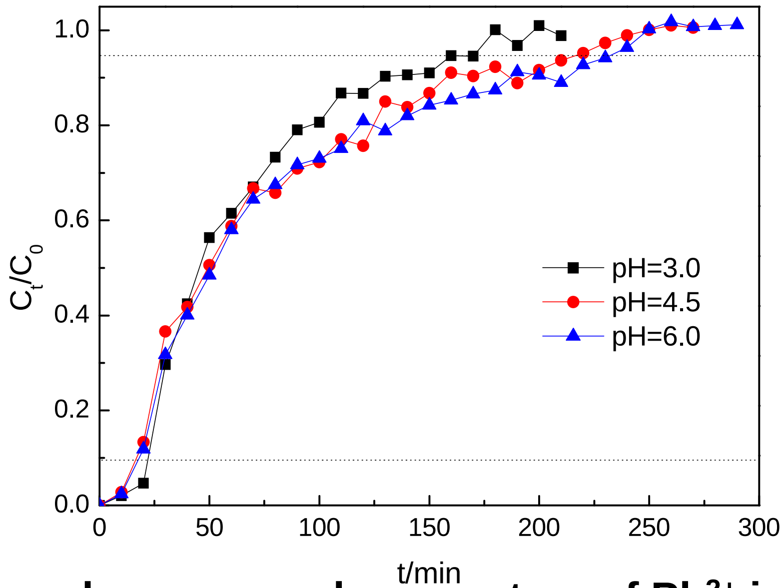


Figure 1 The breakthrough curves and parameters of Pb^{2+} ion in fixed-bed adsorption system under impact of pH.

pH	t_b/(min)	t_e/(min)	M_{ad}/(mmol)	M_{tatol}/(mmol)	q_d/(mmol/g)	H/(cm)	R/%
3.0	22.13	169.99	0.1659	0.4309	0.0553	27.11	38.51
4.5	18.30	217.13	0.1915	0.5504	0.0638	31.59	34.79
6.0	16.92	232.37	0.2195	0.5891	0.0732	29.86	37.26

3. Results and Discussion

3.2 Breakthrough curve of Pb^{2+} ion adsorption process under different contaminants

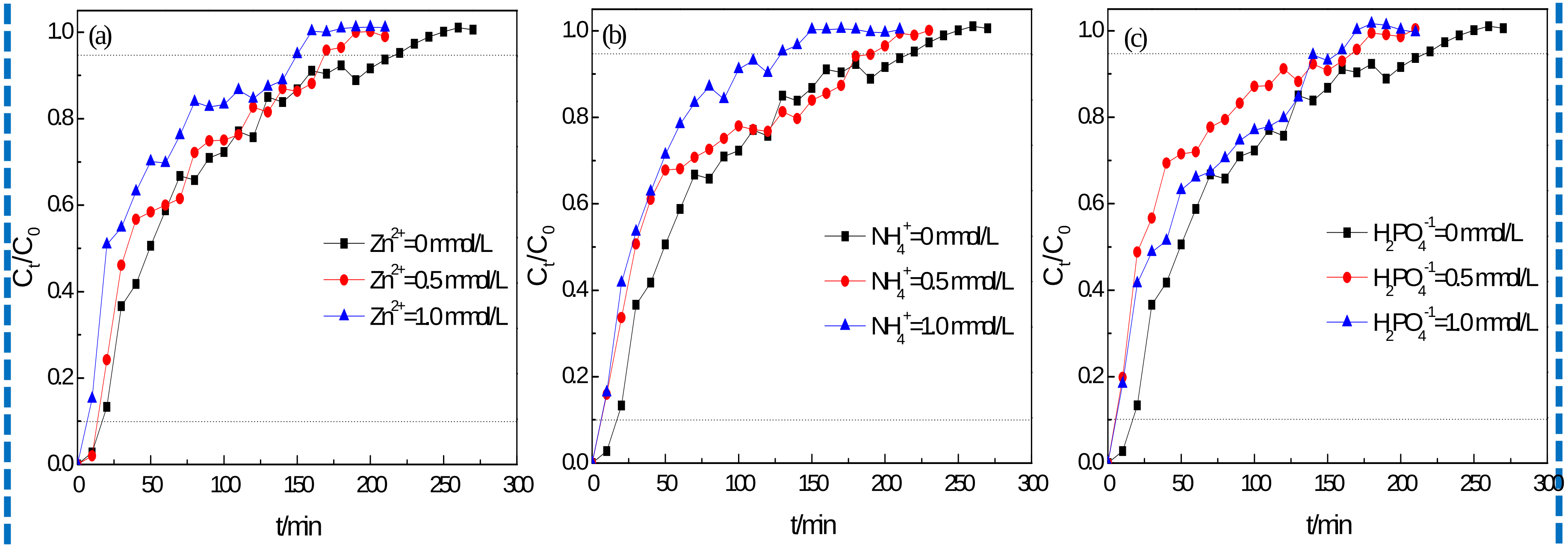
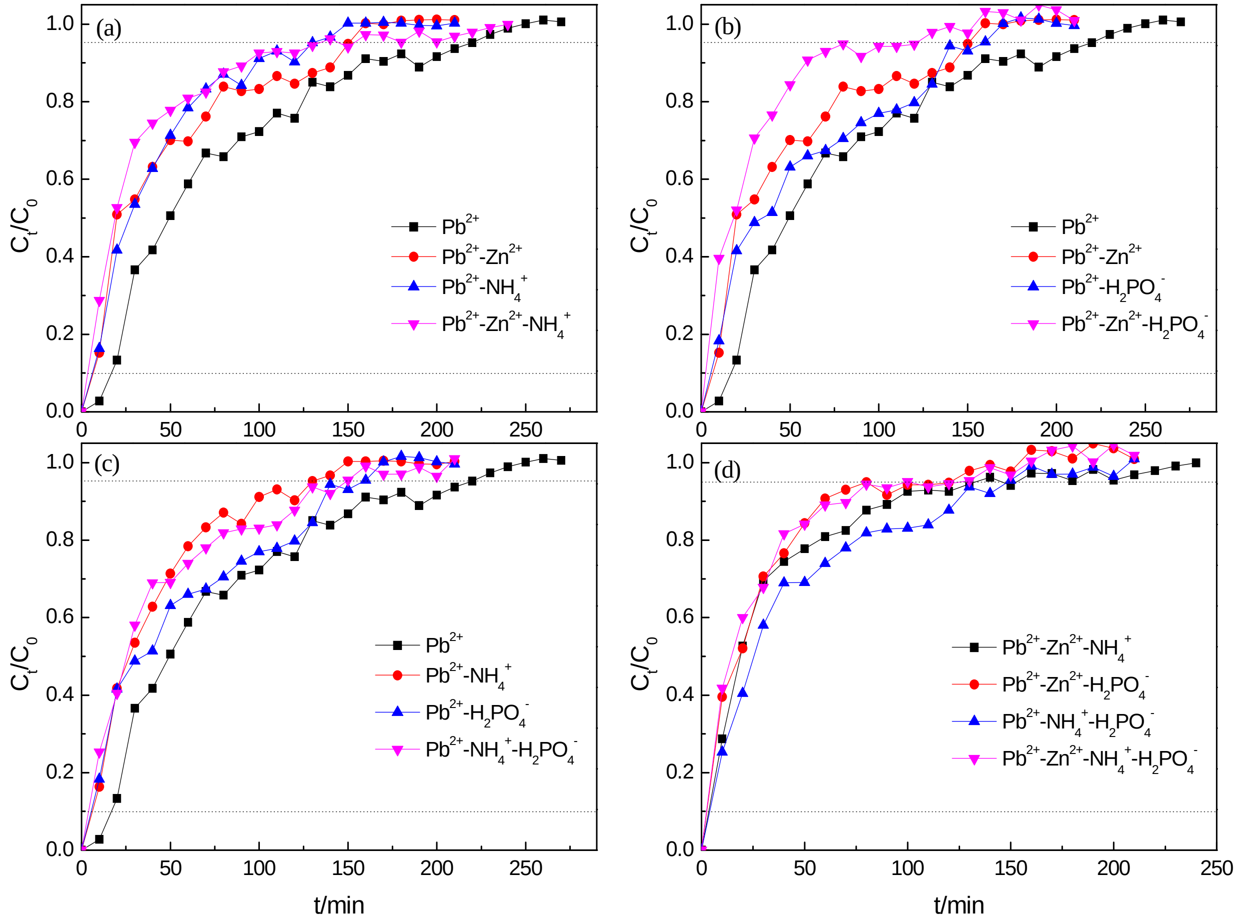


Figure 2 The breakthrough curves of Pb^{2+} ion in fixed-bed system under impact of Zn^{2+}, NH_4^+, and $H_2PO_4^-$

3.3 Breakthrough curve of Pb^{2+} ion adsorption process under different contaminants



①Pb^{2+}-Zn^{2+}-NH_4^+
②Pb^{2+}-Zn^{2+}-$H_2PO_4^-$
③Pb^{2+}-NH_4^+-$H_2PO_4^-$
④Pb^{2+}-Zn^{2+}-NH_4^+-$H_2PO_4^-$

The adsorption capacity :④>②>①>③.

The existence of $H_2PO_4^-$ ion reduced the impact of coexisting contaminations in fixed-bed.

On the contrary, the multiple systems containing Zn^{2+} ion showed more inhibition effect. This phenomenon implied that rational simultaneous dispose of different contaminations may helpful to promote effective in treatment technology.

3.2 Breakthrough curve of Pb^{2+} ion adsorption process under different contaminants

Table 2 The breakthrough curve parameters and variations of Pb^{2+} under impact of Zn^{2+}, NH_4^+, and $H_2PO_4^-$

System	co-existence ions concentration/ mmol/L	t_b/ min	t_e/ min	M_{ad}/ mmol	M_{tatol}/ mmol	R/ %	Δt_b/ min	Δt_e/ min	ΔM_{ad}/ mmol	ΔM_{tatol}/ mmol	ΔR/ %
Pb^{2+}	-	18.30	217.13	0.1915	0.5504	34.79	-	-	-	-	-
Pb^{2+}-Zn^{2+}	0.5	13.98	169.12	0.1855	0.4287	42.07	-4.32	-48.01	-0.0060	-0.1217	7.28
	1.0	6.90	150.06	0.1546	0.3804	39.52	-11.40	-67.07	-0.0369	-0.1700	4.73
Pb^{2+}-NH_4^+	0.5	6.33	192.56	0.1893	0.5297	35.73	-11.97	-24.57	-0.0022	-0.0207	0.94
	1.0	6.08	129.82	0.1582	0.3571	44.29	-12.22	-87.31	-0.0333	-0.1933	9.50
Pb^{2+}-$H_2PO_4^-$	0.5	5.64	158.27	0.1024	0.4354	23.51	-12.66	-58.86	-0.0891	-0.1150	-11.28
	1.0	5.13	167.43	0.1405	0.4606	30.50	-13.17	-49.70	-0.0510	-0.0898	-4.29
Pb^{2+}-Zn^{2+}-NH_4^+	1.0/1.0	3.34	132.34	0.0778	0.3641	21.37	-14.96	-84.79	-0.1137	-0.1864	-13.42
Pb^{2+}-Zn^{2+}-$H_2PO_4^-$	1.0/1.0	2.85	121.55	0.0364	0.3344	10.88	-15.45	-95.58	-0.1551	-0.2160	-23.91
Pb^{2+}-NH_4^+-$H_2PO_4^-$	1.0/1.0	4.07	148.98	0.1087	0.4098	26.53	-14.23	-68.15	-0.0828	-0.1406	-8.26
Pb^{2+}-Zn^{2+}-NH_4^+-$H_2PO_4^-$	1.0/1.0/1.0	2.40	126.93	0.0626	0.3492	17.92	-15.90	-90.20	-0.1289	-0.2012	-16.87

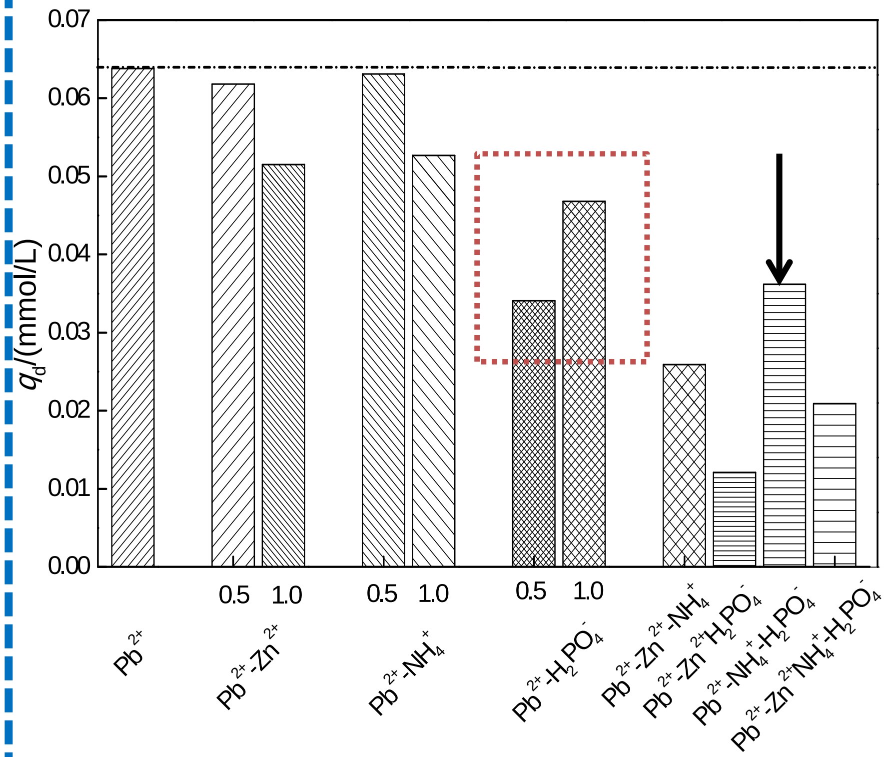


Figure 4 The dynamic adsorption capacity (q_d) of fixed-bed in different systems

Dynamic adsorption capacity (q_d) and **the height of mass transfer zone (H)** represent the adsorption performance of unit mass and unit volume, respectively, and they can be used to describe the adsorption capacity of fixed-bed.

Contrast study of q_d and H under the effect of different factors is help to better understand the quantitative influence of contaminations on fixed-bed system.

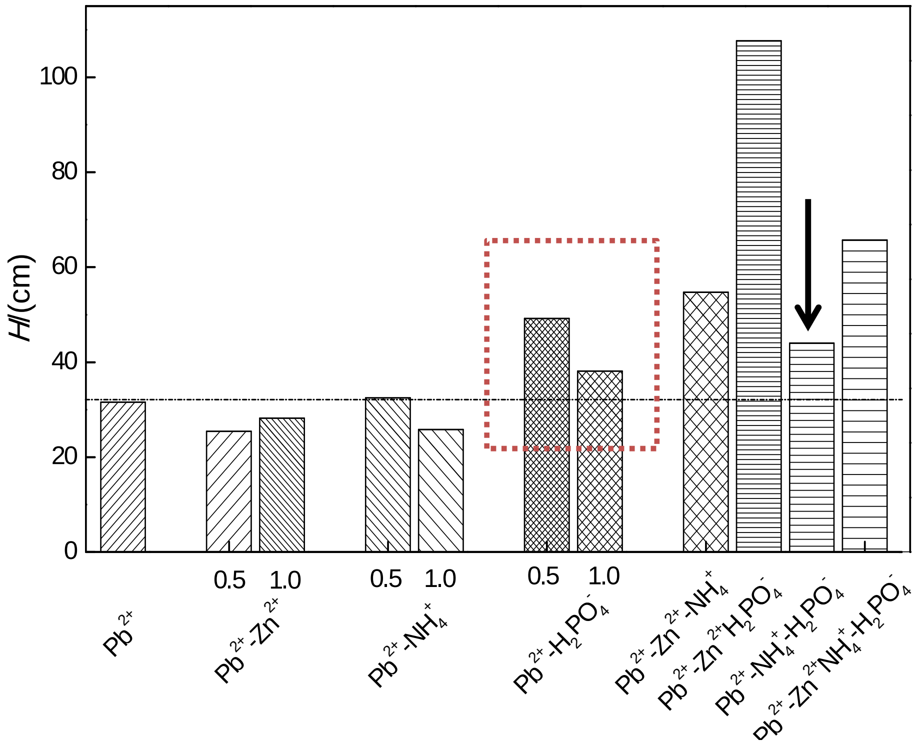


Figure 5 The height of transfer zone (*H*) of fixed-bed in different systems

By comparing the Figure 4 and 5, the results indicated that the variation of *H* showed **opposite tendency** to that of q_d in the corresponding systems, and the fixed-bed need more adsorbent to adsorb unit mass Pb^{2+} ion in the effect of multiple contaminations.

But under the **Pb^{2+}-NH_4^+-$H_2PO_4^-$** system, compared to the other ternary-solute and quarternary-solute solutions, the *H* and q_d showed distinct advantage. In this situation, the inhibition effect on SBB was minimal.

This result demonstrated that the simultaneous treatment of **Pb^{2+}, NH_4^+, and $H_2PO_4^-$** in fixed-bed system maybe a viable method.

3.3 The fitting curves of Thomas model(a, b, c) and Yoon-Nelson model (d, e, f) for breakthrough curves

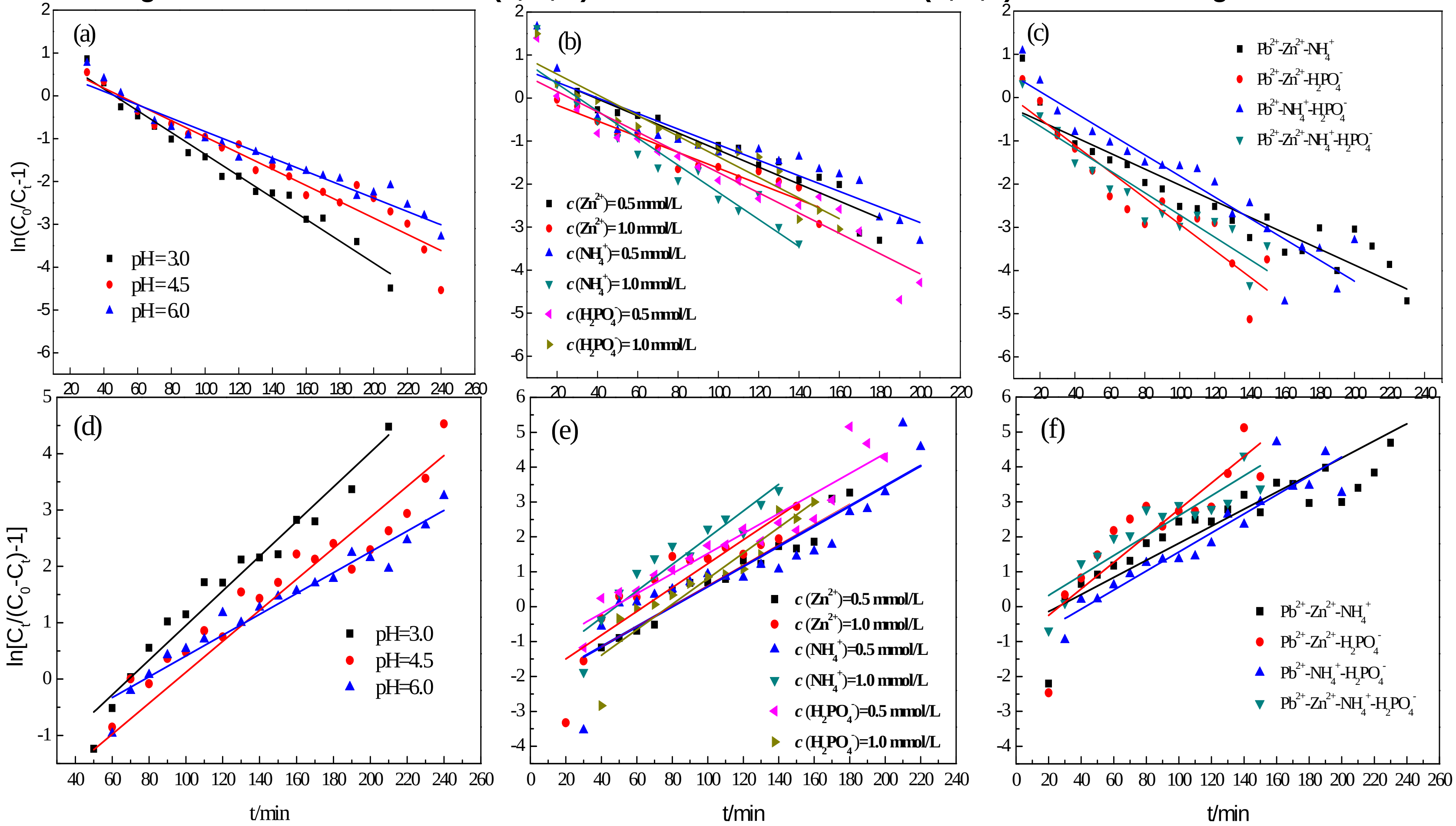


Table 3 The parameters of Thomas model and Yoon-Nelson model

System	co-existence ions concentration	Thomas model			Yoon-Nelson model		
		K_{Th}	q_{md}	R^2	K_{YN}	τ	R^2
Pb^{2+}	pH=3.0	0.0301	0.0391	0.9738	0.0314	69.55	0.9396
	pH=4.5	0.0225	0.0522	0.9788	0.0275	95.50	0.8403
	pH=6.0	0.0185	0.0636	0.9704	0.0185	77.55	0.9485
Pb^{2+}-Zn^{2+}	0.5	0.0234	0.0330	0.9205	0.0293	74.54	0.9515
	1.0	0.0217	0.0093	0.9253	0.0341	63.98	0.7990
Pb^{2+}-NH_4^+	0.5	0.0197	0.0370	0.8678	0.0279	79.32	0.7918
	1.0	0.0344	0.0281	0.9197	0.0341	54.00	0.8767
Pb^{2+}-$H_2PO_4^-$	0.5	0.0256	0.0243	0.9097	0.0287	46.81	0.8925
	1.0	0.0262	0.0396	0.9216	0.0366	78.08	0.8633
Pb^{2+}-Zn^{2+}-NH_4^+	1.0/1.0	0.0202	0.0085	0.8813	0.0244	25.75	0.7853
Pb^{2+}-Zn^{2+}-$H_2PO_4^-$	1.0/1.0	0.0333	0.0035	0.8729	0.0379	26.58	0.7658
Pb^{2+}-NH_4^+-$H_2PO_4^-$	1.0/1.0	0.0266	0.0235	0.8941	0.0272	42.55	0.8867
Pb^{2+}-Zn^{2+}-NH_4^+-$H_2PO_4^-$	1.0/1.0/1.0	0.0280	0.0053	0.8750	0.0286	8.72	0.8323

4. Conclusion

1) The inhibition effect of three categories contaminates on Pb^{2+} adsorption follow the order as $NH_4^+ > Zn^{2+} > H_2PO_4^-$.The complicate contaminations system lead to fixed-bed adsorption performance degradation.

2) When $H_2PO_4^-$ ion exist in ternary or quaternary system, it depressed the inhibition effect of component systems on Pb^{2+} adsorption. And the systems containing Zn^{2+} showed the most significant impact on the breakthrough curves among all combinations,

3) In compared with Yoon-Nelson model, Thomas model can be better used to described the Pb^{2+} adsorption process in fixed-bed system, whereas, the application result was drastically affected by co-existing contaminations.

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THANK YOU!

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