



## Single and coadsorption of copper, cadmium, lead and zinc onto basic oxygen furnace slag

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### ABSTRACT

In this work, single adsorption removal of copper, cadmium, lead, and zinc from aqueous solution by basic oxygen furnace slag (BOFs) which was activated by the mechanochemistry process was investigated. Effects such as initial concentration, contact time, pH, and temperature, as well as adsorption isotherm and kinetics were discussed. The coadsorption capacity of these heavy metals was evaluated. Adsorption mechanism was interpreted by X-ray diffraction and possible reaction path in aqueous solution. In a single metal system, the adsorption equilibrium time was close to 180 min while increasing the initial concentration of adsorbates, pH value, and temperature was in favor of adsorption reaction and increased the maximum adsorption capacity of each metal onto BOFs. Freundlich model was well-fitted than Langmuir in description of adsorption isotherm while the pseudo-second-order model was closer to experimental results. In binary adsorption system, the equilibrium adsorption capacity of coexisting heavy metals Cd(II), Pb(II), and Zn(II) was almost invariably with an increase of initial concentration of Cu(II) in Cu–Cd, Cu–Pb, and Cu–Zn mixed solutions. Cu(II) showed the weak adsorption competitiveness of Cu(II) in the ternary system while the heavy metal competitive adsorption order was Pb(II)>Cd(II)>Zn(II)>Cu(II) in fourfold system. The possible reaction path showed that besides concentration of heavy metals and pH of a solution, the hydrated radius of heavy metal ion and co-efficient of solidity of product formed in the process of precipitation were contributing to adsorption competitiveness of heavy metals.

*Keywords:* Co-adsorption; Basic furnace oxygen slag; Heavy metals; Competitiveness; Mechanism

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### 1. Introduction

The retention of toxic heavy metals from wastewaters is an attractive subject in the field of environmental remediation [1]. Rapid development of industrialization resulted in generation of large quantities of wastewater containing Cr(III,VI), As(III,V), Cd(II), Pb(II), Cu(II), Zn(II), and Hg(II), which are particularly dangerous for the environment and human [2]. Among these heavy metals, many technologies have been used in the treatment of the heavy metal contaminated waters, such as ion-exchange [3], chemical precipitation [4], membrane [5], complexation [6], electrochemical

treatment [7] and adsorption [8]. The adsorption is regarded as a very effective and economical process for the treatment of wastewaters. Consequently, a low-cost and highly efficient adsorbents produced from industrial solid waste is necessary to the removal of heavy metals from aqueous solution by adsorption. It should be noted that many kinds of waste such as agricultural and industrial have been used for wastewater treatment as low-cost sorbents [9,10].

Now a day, many studies have shown that basic oxygen furnace slag (BOFs) can be effectively used to remove heavy metal. Even in the strong acid aqueous solution, BOFs can be regarded as effective adsorbents due to their higher acid neutralization capacity when compared with other adsorbents [11]. BOFs containing calcium,

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magnesium, alumina, and iron chemical compounds usually generated from the BOFs steel making process [12,13]. The heterogeneity of the BOFs surface stemmed from two sources, namely geometrical and chemical [14], which highly contribute to the unique adsorption properties of BOFs and make it as a low-cost adsorbent for removal of substances from wastewater. For removing single adsorbate, many researches have been conducted on adsorption removal heavy metals ions such as Cu [11,15], Cd [16], Pb [17], and Zn [18] by steel slag. The effect of ion exchange, surface coordination, and chemical precipitation was used to describe the removal mechanism of heavy metals onto BOFs [19]. The ion exchange occurs between metal cations and calcium ion on the BOFs surface [19,20]. Metal cations reacted with a hydroxyl group produced from the dissociation reaction showed the surface coordination effect [11,19]. Hydroxyl generated by hydrolysis of BOFs, which can react with metal ions by produce metal hydroxides, facilitate to removal of heavy metal by the effect of chemical precipitation [16,19,20]. On the other hand, it is noted that heavy metal adsorption depends on adsorbent characteristics as well as the nature of the various heavy metal ions. It is concluded that adsorption behavior is very different when multi heavy metals coexist in aqueous solution compared to single adsorption [21]. However, there are few kinds of literatures related to coadsorption heavy metals in binary, ternary even the fourfold adsorbates system by BOFs as adsorbent. Consequently, it suggests that the coadsorption capacity and removal mechanisms of coexisting heavy metal ions in solutions by BOFs are still unknown. As noted, the wastewater generated from many sources such as waste mines, tailings, electroplating sludge often contains various heavy metal ions [22–24]. BOFs as an adsorbent has been proved that it is either low-cost or efficient for adsorption removal of some kinds of single heavy metal ion in aqueous solution. Adsorption equilibrium capacity, in addition to the possible reaction path, is not clear when multi heavy metal ions are removed by BOFs in an aqueous solution. The coadsorption mechanism of coexisting heavy metals has not yet to be established. Therefore, it is very important to understand the simultaneous removal behavior of various heavy metals that coexist in the wastewater.

In this present work, BOFs adsorbent was facilely prepared by grinding and was used to removal coexisting Cu(II), Cd(II), Pb(II) and Zn(II) from aqueous solution. Based on the understanding of the adsorption behavior of single

heavy metal ion, the simultaneous removal behavior of coexisting these four kinds of heavy metals by BOFs was investigated. The main objectives are: (1) comparing the adsorption capacity of heavy metals between multi- and single system; (2) studying the effect of solution pH and temperature on removal of coexisting heavy metals mentioned above; (3) understanding the mechanism for simultaneous removal of coexisting heavy metals by using analytical techniques and describing the possible reaction path.

## 2. Materials and methods

### 2.1. Materials

BOFs were collected from the Wuhan Iron Steel Group. These slags were stockpiling and setting for two years. An X-ray fluorescence spectrometer (XRF-1800, Shimadzu, Japan) was used for chemical compositions analysis. A Blain specific surface area meter (Shanghai, China) was used for the evaluation of specific surface area of BOFs. A laser particle size analyzer (LS800, OMEC) was used to determine the  $D_{50}$  of BOFs. Parts of physical properties are listed in Table 1. The sieve size of BOFs was controlled under 0.6 mm as original materials. Then the original BOFs were activated by mechanochemistry treatment. Two BOF powders were used as adsorbents in this work. ST1 and ST2 referred the adsorbents ground for 1 h by a vertical planetary ball mill (QM-1SP2 Model). Artificial wastewater was synthesized by dissolving analytical grade chemicals, such as copper nitrate, cadmium nitrate, lead nitrate, and zinc nitrate into deionized water.

### 2.2. Methods

#### 2.2.1. Adsorption batch experiment

Both single and multi-heavy metals adsorption experiments were conducted to determine the adsorption characteristics of BOFs for the heavy metals. In the single heavy metal adsorption batch experiment, accurately weighed 0.500 g (solid–liquid ratio of 5 g L<sup>-1</sup>) BOFs was added into each flask and shaken in a shaker with temperature adjuster (Orbital Model SHZ-88, China) with a vibration speed of 150 rpm. To understand the adsorption isotherm of BOFs, preliminary adsorption experiments were performed at 20°C to determine the contact time required to attain equilibrium. A series of 250 mL Erlenmeyer flask filled with 100 mL Cu(II), Cd(II), Pb(II), and Zn(II) solution with concentration varied

Table 1  
Main chemical composition and properties of BOFs

Chemical composition/%		Physical properties		
		Samples	ST1	ST2
SiO <sub>2</sub>	13.75	Bulk density/g cm <sup>-3</sup>	3.09	3.13
CaO	45.462	D <sub>50</sub> /mm	4.38	7.85
MgO	6.211	Blain surface area/m <sup>2</sup> kg <sup>-1</sup>	405	534
Al <sub>2</sub> O <sub>3</sub>	3.74	Total porosity/%	5.56	6.15
Total Fe <sup>a</sup>	21.78	Percentage of mesoporous (pore size 2–50 nm)/%	47.8	54.3

<sup>a</sup>means total content of Fe<sub>2</sub>O<sub>3</sub> and FeO by mass.

from 1,000 to 3,000 mg L<sup>-1</sup>. Batch adsorption experiments were carried out by shaking a series of bottles for 6 h, and then standing stored for 3 h before filtering. To understand adsorption kinetics of BOFs, a series of bottles with 0.500 g adsorbent and 100 mL solution with Cu(II), Cd(II), Pb(II), and Zn(II) concentration of 2,000 mg L<sup>-1</sup>, then mixed and shook for different contact time and then keeping stored for 3 h under room temperature before filtering. After the reaction, 10 ml of the solution was centrifuged at 3,500 rpm for 15 min. The filtrate was collected and the concentration of Cu(II), Cd(II), Pb(II), and Zn(II) was analyzed by the atomic absorption spectrometer (TAS 990 Model, Beijing, China) or ICP-AES (Optima 4300DV, PerkinElmer, USA). The effect of pH on adsorption was carried out. A batch of experiments with 1,000 mg L<sup>-1</sup> of initial concentration and 0.500 g adsorbent was conducted with increasing pH values from 3.0 to 12. Solution of 0.1 M NaOH and 0.1 M HNO<sub>3</sub> were used for pH adjustment by a pH control measurement (PHS-3C Model). The effect of temperature on adsorption was conducted under various temperatures (293.15 K to 333.15 K in Kelvin temperature). In this work, the ionic strength was adjusted by NaCl and maintained by 0.1 M in all solutions.

In the coadsorption batch experiments, adsorption capacity in the binary, ternary, and fourfold heavy metals system was investigated. ST2 was used as an adsorbent in the coadsorption experiment. Coadsorption experiments were performed at 20°C. Only the effect of pH value on the maximum adsorption capacity of each heavy metal was investigated. In a binary system, a series of coadsorption experiments were conducted by maintaining the concentration of the coexisting adsorbates, such as Cd(II), Pb(II), and Zn(II) while changing the concentration of the main adsorbate Cu(II) constant. By mixing Cu(II) solution with the different coexisting heavy metal solutions according to the relative volume ratio, the initial concentration of the coexisting adsorbates was 500 mg L<sup>-1</sup> while the concentration of the main adsorbate Cu(II) varied from 500 to 1,500 mg L<sup>-1</sup>. In the ternary and fourfold system, the initial concentration of each heavy metals was 500 mg L<sup>-1</sup>. The total volume of the mixing solution was keeping 100 ml. The procedure of adsorption, filtration, and determination of the concentration of each heavy metal was carried out as mentioned above. All the adsorption tests were repeated twice and the average value of measurements was reported.

### 2.2.2. Adsorption models and equations

The equilibrium concentration (equilibrium adsorption capacity) of heavy metals was calculated according to the following equations:

$$q_e = (C_0 - C_e) \frac{V_0}{m} \quad (1)$$

where  $C_0$  (mg L<sup>-1</sup>) is the initial concentrations of selected heavy metals;  $C_e$  (mg L<sup>-1</sup>) is the equilibrium concentrations;  $V_0$  (L) is the volume of experiment solutions;  $m$  is the mass of the adsorbent.

Langmuir and Freundlich models were used in this work for description of adsorption isotherm, where Lagergren pseudo-first-order and pseudo-second-order models were

used for analysis of adsorption kinetics. In the thermodynamic equation, the change of Gibb's free energy, entropy, and heat of adsorption were calculated, as well as adsorption activation energy. These models and their learner regression models have been described by previous literature [11], which were not introduced in this work.

### 2.2.3. Characterization methods

To understand the mechanism of single and coadsorption of heavy metals onto BOFs, the residues containing adsorbent and adsorbates were separated from solutions first and dried in an oven with a temperature of 85°C for 24 h. X-ray diffraction (XRD) patterns were analyzed to identify the phase composition and crystal structure of the samples combined with heavy metals by the D-Max/RB Model XRD Analyzer (Rigaku, Japan). Before and after the adsorption reaction, the functional groups of BOFs were analyzed by Fourier transform infrared spectroscopy (FTIR, Nexus, Thermo Nicolet, USA).

## 3. Results and discussion

### 3.1. Adsorption characteristics in a single heavy metal system

#### 3.1.1. Effect of contact time

Fig. 1 shows the effect of contact time on the single adsorption capacity of the Cu(II), Cd(II), Pb(II), and Zn(II) by the ST1 and ST2. As can be seen, ST1 and ST2 with a dosage of 5.0 g L<sup>-1</sup> can effectively remove Cu(II), Cd(II), Pb(II), and Zn(II) from single heavy metal aqueous solution. Adsorption equilibrium can be obtained within 180 min. A higher removal rate of all heavy metals can be obtained during the first 15 min of reaction time. The adsorption equilibrium was achieved after reaction for 3 h. The adsorption capacity by ST1 and ST2 at 3 h of adsorption time was in order of Pb(II) > Cd(II) > Zn(II) > Cu(II). It indicated that in a single heavy metal system, BOFs adsorbents showed higher removal efficiency of Pb(II). The removal capacity was 399.67 mg g<sup>-1</sup>. While a slightly lower removal rate of Cu(II) was obtained combined with the removal capacity of 391.39 mg g<sup>-1</sup>.

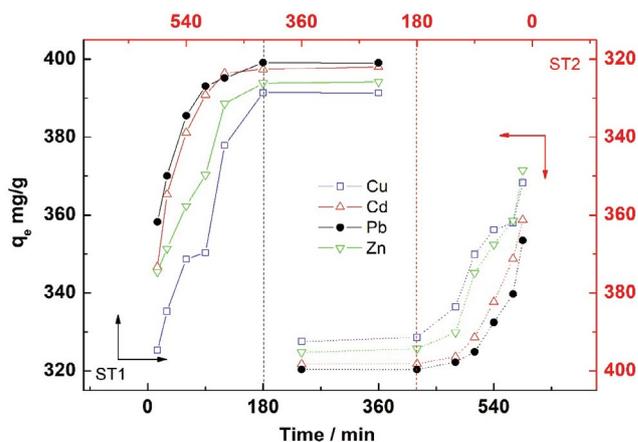


Fig. 1. Effect of contact time on single adsorption of Cu(II), Cd(II), Pb(II), and Zn(II) on ST1 and ST2.

Compared with ST1, ST2 showed the higher removal efficiency of all heavy metals. This was contributed to the higher surface area, hydration reaction activity of mineral composition because of the effect of mechanochemistry on the activation of BOFs. This modification of adsorbent which facilitated the adsorption of heavy metals was reported in many types of research [25].

### 3.1.2. Effect of initial concentration

Fig. 2 shows the effect of initial concentration on the single adsorption capacity of the Cu(II), Cd(II), Pb(II), and Zn(II) by the ST1 and ST2 increasing initial concentration of heavy metals, the increment of the equilibrium adsorption capacity slowed down. Generally, increasing the initial concentration would increase adsorption capacities. It was concluded that BOF adsorbent reached the equilibrium adsorption capacity in the tested range of initial concentration of heavy metal. The maximum capacity of Cu(II), Cd(II), Pb(II), and Zn(II) onto ST2 was 491.13, 503.35, 525.58, and 510.07 mg g<sup>-1</sup>, respectively. Based on the sorption classification system, it can be predicted that single adsorption isotherms of Cu(II), Cd(II), Pb(II), and Zn(II) onto BOFs were L-1 type.

### 3.1.3. Effect of pH

Fig. 3 shows the effect of pH on the single adsorption capacity of the Cu(II), Cd(II), Pb(II), and Zn(II) by the ST1 and ST2. The removal efficiency was lower in the solutions with lower pH value but readily increased as the initial pH value increasing before the equilibrium state. These results were consistent with findings published in other researches. Compared to heavy metal ions, H<sup>+</sup> strongly bonds to active sites onto the surface of BOFs in solution with a lower pH value. During the hydrolysis and ionization reactions of BOFs, OH<sup>-</sup> released from calcium and magnesium-containing compounds, resulting in the consumption and neutralization of H<sup>+</sup> in aqueous solutions [16,26]. It is reported that positively charged sites on the surface increased with an increase of pH, indicating that adsorption of the positively charged heavy metal ions was enhanced due to electrostatic

attraction [19,27,28]. Duan and Su [16] reported that chemical precipitation facilitates to removal of heavy metal ions when the value of pH is beyond 7. In this work, as the initial pH increased and was beyond 8, the removal efficiency of Cu(II), Cd(II), Pb(II), and Zn(II) by ST1 and ST2 was slowly increased. When pH value was lower than 6, the reaction between heavy metals and BOFs was mainly contributed to ion exchange with H<sup>+</sup>, while adsorbent reacted with heavy metals in the manner of metal hydroxyl complexes in the solution of higher pH value.

### 3.1.4. Effect of temperature

Fig. 4 shows the effect of temperature on the single adsorption capacity of the Cu(II), Cd(II), Pb(II), and Zn(II) by the ST1 and ST2. With increasing temperature, the removal efficiency of all heavy metals increased. This might contribute to the increase of entropy value caused by desorption of water molecules was higher than the decrease of entropy value by adsorbing heavy metals onto the adsorbents during the reaction between Cu(II), Cd(II), Pb(II), and Zn(II) with

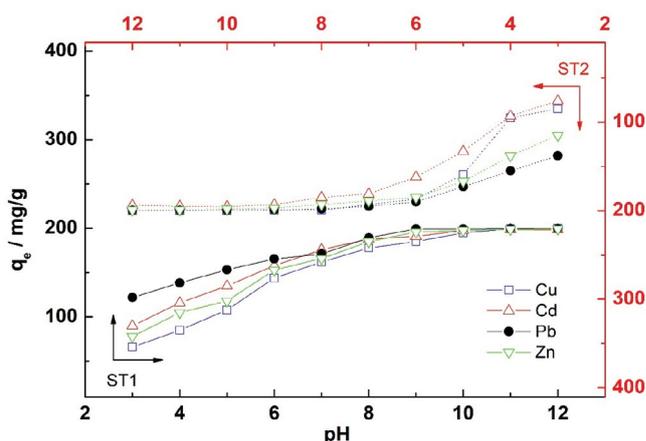


Fig. 3. Effect of pH on single adsorption of Cu(II), Cd(II), Pb(II), and Zn(II) on ST1 and ST2.

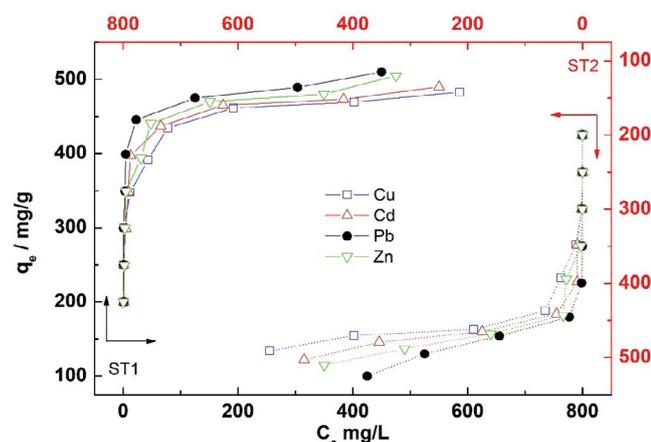


Fig. 2. Effect of initial concentration on single adsorption of Cu(II), Cd(II), Pb(II), and Zn(II) on ST1 and ST2.

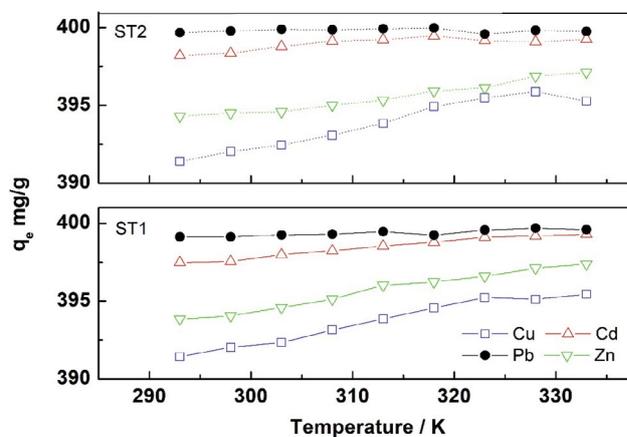


Fig. 4. Effect of temperature on single adsorption of Cu(II), Cd(II), Pb(II), and Zn(II) on ST1 and ST2.

BOFs in aqueous solutions [29,30]. This resulted in the endothermic process of adsorption Cu(II), Cd(II), Pb(II), and Zn(II) onto BOFs. Therefore, it indicated that increasing the temperature was in favor of adsorption reaction and increased the maximum adsorption capacity of each metal onto BOFs. Differently, the adsorption capacity of Cu(II) and Zn(II) significantly increased, which showed adsorption of Cu(II) and Zn(II) onto BOFs was easily influenced by increasing reaction temperature.

### 3.1.5. Single adsorption models

According to single adsorption results, ST2 was selected as an adsorbent in the understanding of the adsorption isotherm, kinetics, and thermodynamics. Equations and parameters are listed in Tables 2 and 3. Adsorption isotherm results showed that the Freundlich model was well-fitted than Langmuir. This indicated that there were not only adsorption heavy metals onto the monolayer of BOFs, but also the heterogeneous pores or surfaces as main adsorption sites. In our previous study [11], precipitation of oxides from BOFs in aqueous solution would interfere with the linear regression in the description of either Langmuir or Freundlich isotherm models. Higher initial concentration of heavy metals resulted in the occurrence of combined removal effects provided by adsorption and precipitation. Besides, the heterogeneous surface structure and composition of BOFs led to an inaccurate description of adsorption isotherm of heavy metals [14].

Results in Table 3 showed the pseudo-first-order and pseudo-second-order models well described the kinetic process of adsorption Cu(II), Cd(II), Pb(II), and Zn(II) onto BOFs. The predicted maximum adsorption capacities by the pseudo-second-order model was closer to experiment results, compared with pseudo-first-order model. The pseudo-second-order kinetics model is determined by the adsorption capacity of a solid surface of BOFs. It is noted that surface adsorption capacity is highly related to the number of surface reaction sites. Compared with the pseudo-first-order model, the pseudo-second-order kinetics model is the predominant mechanism based on chemical adsorption in this work [31].

Since adsorption is an exothermic process, it would be expected that an increase in the temperature would result in a decrease in the adsorption capacity. In this work, the adsorption capacity increased with an increase in temperature. This was mainly because the precipitation process or the intra-particle transport-pore of the adsorbent diffusion process was endothermic [29,32,33]. Based on results presented in Table 4,  $\Delta G^\circ$  was negative while decreasing with an increase of temperature, which indicated that adsorption reaction of Cu(II), Cd(II), Pb(II), and Zn(II) onto BOFs was spontaneous under the higher reaction temperature. Positive value of  $\Delta H^\circ$  and  $\Delta S^\circ$  meant the change of combining structure between adsorbates and adsorbents while increasing temperature was conducive to the spontaneous process of adsorption reaction [11].

Table 2  
Adsorption isotherm equations of Cu(II), Cd(II), Pb(II), and Zn(II) onto ST2

Isotherm	Langmuir: $q_e = \frac{q_m b C_e}{1 + b C_e}$			Freundlich: $q_e = K_F C_e^{1/n}$		
	$q_m$	$b$	$R^2$	$K_F$	$n$	$R^2$
ST2-Cu	424.6	5.98	0.7404	278.9	0.093	0.9785
ST2-Cd	442.5	2.49	0.7127	283.1	0.097	0.9119
ST2-Pb	483.0	2.94	0.8517	314.6	0.086	0.9171
ST2-Zn	441.2	9.23	0.7729	302.8	0.087	0.9679

Table 3  
Kinetics parameters of single adsorption of Cu(II), Cd(II), Pb(II), and Zn(II) onto ST2

Kinetics	$q_{e,exp}/\text{mg g}^{-1}$	Pseudo-first-order kinetic model $\ln(q_e - q_t) = \ln q_e - k_1 t$			Pseudo-second-order kinetic model $\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$		
		$q_{e,cal}/\text{mg g}^{-1}$	$k_1/\text{min}^{-1}$	$R^2$	$q_{e,cal}/\text{mg g}^{-1}$	$k_2/\text{g mg}^{-1} \text{min}^{-1}$	$R^2$
ST2-Cu	393.0	374.6	0.1243	0.9625	380.2	0.00056	0.9891
ST2-Cd	398.5	379.3	0.1326	0.9890	381.3	0.00059	0.9420
ST2-Pb	399.8	385.1	0.1254	0.9595	391.0	0.00061	0.9871
ST2-Zn	395.5	380.2	0.0930	0.9320	390.5	0.00040	0.9897

Table 4  
Thermodynamics parameters of single adsorption of Cu(II), Cd(II), Pb(II), and Zn(II) onto ST2

	$E/\text{kJ mol}^{-1}$	$\Delta H^\circ/\text{kJ mol}^{-1}$	$\Delta S^\circ/\text{J mol}^{-1} \text{K}^{-1}$	$\Delta G^\circ/\text{kJ mol}^{-1}$				
				293 K	303 K	313 K	323 K	333 K
ST2-Cu	28.0	33.2	154.9	-12.2	-13.7	-15.3	-16.8	-18.4
ST2-Cd	16.9	71.8	317.7	-21.3	-24.5	-27.6	-30.8	-34.0
ST2-Pb	36.6	109.2	657.2	-31.0	-37.5	-44.1	-50.7	-57.2
ST2-Zn	16.9	33.1	161.5	-14.2	-15.8	-17.4	-19.1	-20.7

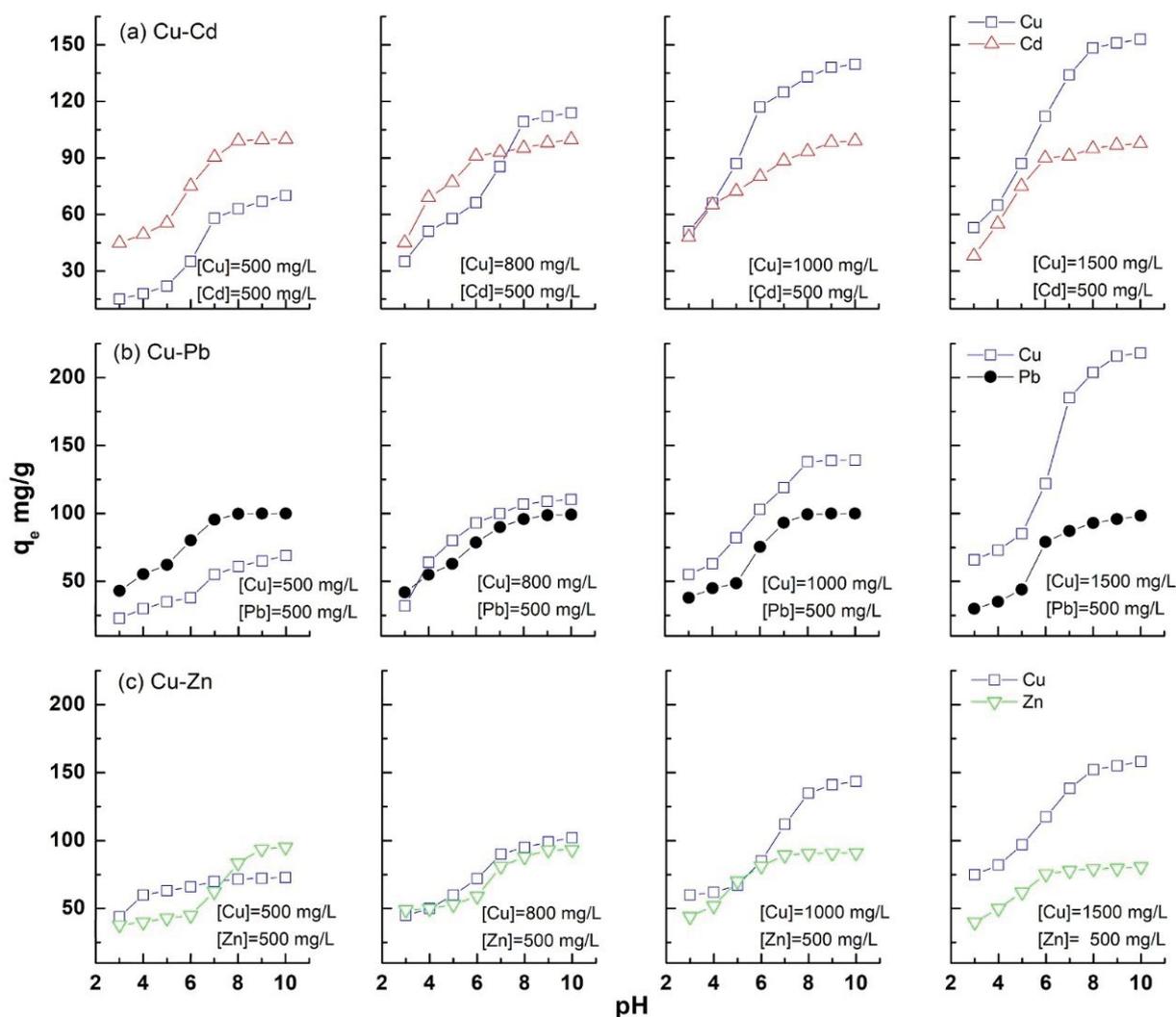


Fig. 5. Coadsorption equilibrium capacity of Cu(II), Cd(II), Pb(II), and Zn(II) on ST1 and ST2 in the binary system.

### 3.2. Coadsorption equilibrium capacity

#### 3.2.1. Coadsorption in binary system

Fig. 5 shows the coadsorption equilibrium capacity of the Cu(II), Cd(II), Pb(II), and Zn(II) by the ST2 in the binary system under the different pH values of the solution. In Cu–Cd mixed solution, with an increase of the concentration of Cu(II), the adsorption capacity of Cu(II) onto ST2 increased.

The maximum adsorption capacity in the Cu–Cd system (Fig. 5a) was significantly lower than that in a single metal solution. When the initial concentration of Cd(II) and Cu(II) was 500 and 1,500 mg L<sup>-1</sup>, respectively, the maximum adsorption capacity of Cu(II) decreased from 299.7 mg g<sup>-1</sup> (single metal) to 152.9 mg g<sup>-1</sup>, while the maximum adsorption capacity of Cd(II) was 97.7 mg g<sup>-1</sup>. This indicated that the maximum adsorption capacity of Cu(II) was significantly influenced

by coexisting with Cd(II). When the initial concentration of both Cd(II) and Cu(II) was 500 mg L<sup>-1</sup>, the maximum adsorption capacity of Cd(II) was higher than that of Cu(II). This indicated that the adsorption competitiveness of Cd(II) was stronger than that of Cu(II). In Fig. 5b, compared to the single adsorption results, existence of Pb(II) led to the decrease of the maximum adsorption capacity of Cu(II) and Pb(II) showed the higher adsorption competitiveness than that of Cu(II) when the initial concentration of these two heavy metals was both 500 mg L<sup>-1</sup>. When the initial concentration of Pb(II) and Cu(II) was 500 and 1,500 mg L<sup>-1</sup> respectively, the maximum adsorption capacity of Cu(II) decreased from 299.7 mg g<sup>-1</sup> (single metal) to 217.9 mg g<sup>-1</sup>, while the maximum adsorption capacity of Pb(II) was 98.3 mg g<sup>-1</sup>. It can be seen from Fig. 5c that Cu(II) is more competitive than Zn(II) at lower pH and the same initial concentration of Zn(II) and Cu(II). When the initial concentration of Zn(II) and Cu(II) was 500 and 1,500 mg L<sup>-1</sup> respectively, the maximum adsorption capacity of Cu(II) decreased from 299.7 mg g<sup>-1</sup> (single metal) to 158.3 mg g<sup>-1</sup>, while the maximum adsorption capacity of Pb(II) was 80.7 mg g<sup>-1</sup>. In Cu–Cd, Cu–Pb, and Cu–Zn mixed solutions, the equilibrium adsorption capacity of coexisting heavy metals Cd(II), Pb(II), and Zn(II) was almost invariably with an increase of initial concentration of Cu(II). With an increase of pH value, the adsorption capacity of heavy metals in the mixed solution system increased, which was consistent with the change rules in a single heavy metal system. The meanwhile, the adsorption capacity of each heavy metal in a binary system was significantly lower than that in a single heavy metal solution respectively under the same initial concentration.

### 3.2.2. Coadsorption in ternary and fourfold system

Fig. 6 shows the coadsorption equilibrium capacity of the Cu(II), Cd(II), Pb(II), and Zn(II) by the ST2 in ternary and fourfold system under the different pH value of the solution. In the ternary system, the initial concentration of each heavy metal was 500 mg L<sup>-1</sup>. Compared to the single adsorption results, coexisting with the other two heavy metals led to the decrease of the maximum adsorption capacity of Cu(II), which showed the weak adsorption competitiveness of Cu(II) in the ternary system. Cd(II) and Pb(II) showed more competitive adsorption capacity when coexisted with Cu(II) and Zn(II). When Cu(II), Cd(II), Pb(II), and Zn(II)

coexisting in mixed solution, the adsorption capacity was in an order of Pb(II) > Cd(II) > Zn(II) > Cu(II). With an increase of initial pH value of the mixed solution, the coadsorption of these heavy metals reached the equilibrium and the total adsorption capacity by ST2 was 352.9 mg g<sup>-1</sup>. Combined with the coadsorption results in a binary system, it indicated that adsorption in single and multi-heavy metal systems were necessary to evaluate heavy metal adsorption efficiencies by BOFs. Heavy metals in aqueous solutions rarely occur alone. The transport and fate of heavy metals between aqueous solutions and solid surfaces can be influenced by the associations and interactions of coexisting components. However, many experimental factors influences the adsorption of heavy metal ions onto BOFs, the ratios of metal ions substituted by other competitive metal ions in multi-heavy metal adsorption remained consistent when the metal concentrations changed in a wide range [21,34].

### 3.3. Characterization and mechanism of coadsorption by BOFs

#### 3.3.1. XRD analysis

To clarify the removal behavior of BOFs for single and coadsorption of Cu(II), Cd(II), Pb(II), and Zn(II) in aqueous solutions, The XRD technology was used to characterize the BOFs before and after adsorption reaction. The XRD patterns of dry solid samples before and after the reaction are shown in Fig. 7.

In the single adsorption system, the heavy metal subsistence mainly consisted of phosphates, silicates, hydroxides, and oxides. The exchange of heavy metal ions and other ions in BOFs are usually generated from these four kinds of heavy metal phosphate and silicate. Carbonates were not found in spectra. However, during the hydrolysis and ionization reactions, OH<sup>-</sup> derived from the calcium silicates, calcium oxide, magnesium oxide and other oxides in BOFs, indicating that heavy metal hydroxides can be found in Fig. 7. In the coadsorption system, the main peaks in the spectra were different compared to a single system. Phosphates disappeared while more metal was found in solid oxide solution. It was noted that heavy metals rarely occur alone. The associations and interactions between each other are noted to has the effect on transport and fate of heavy metals from aqueous solutions to solid surfaces, indicating that the adsorption of heavy metal ions is significantly related to environmental

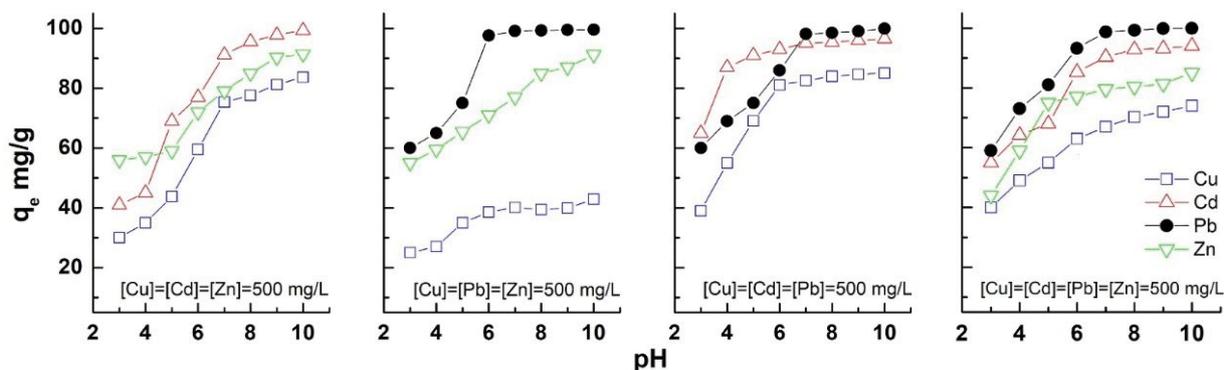


Fig. 6. Coadsorption equilibrium capacity of Cu(II), Cd(II), Pb(II), and Zn(II) on ST1 and ST2 in ternary and fourfold system.

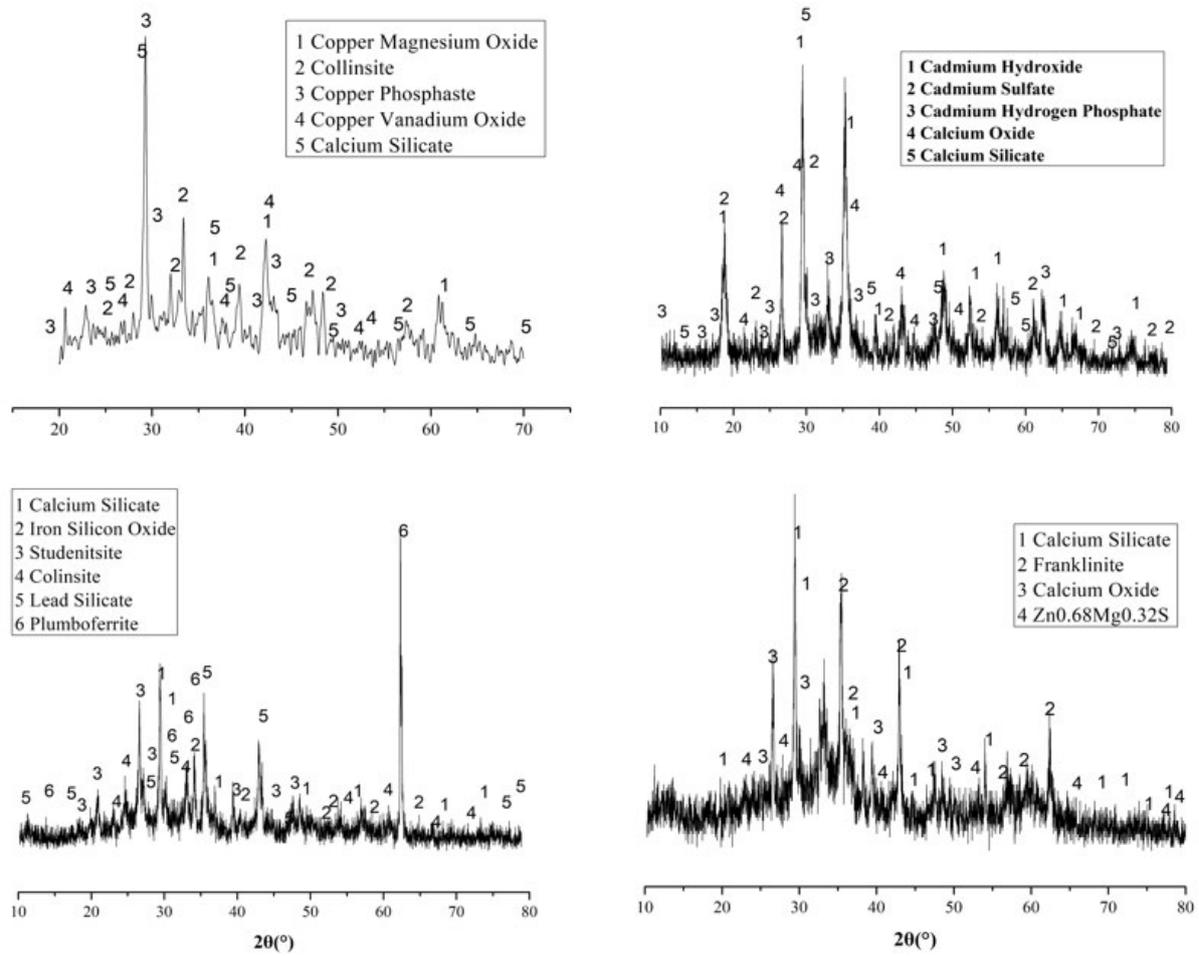


Fig. 7. XRD pattern of Cu(II), (b) Cd(II), (c) Pb(II), and Zn(II) single adsorption onto BOFs.

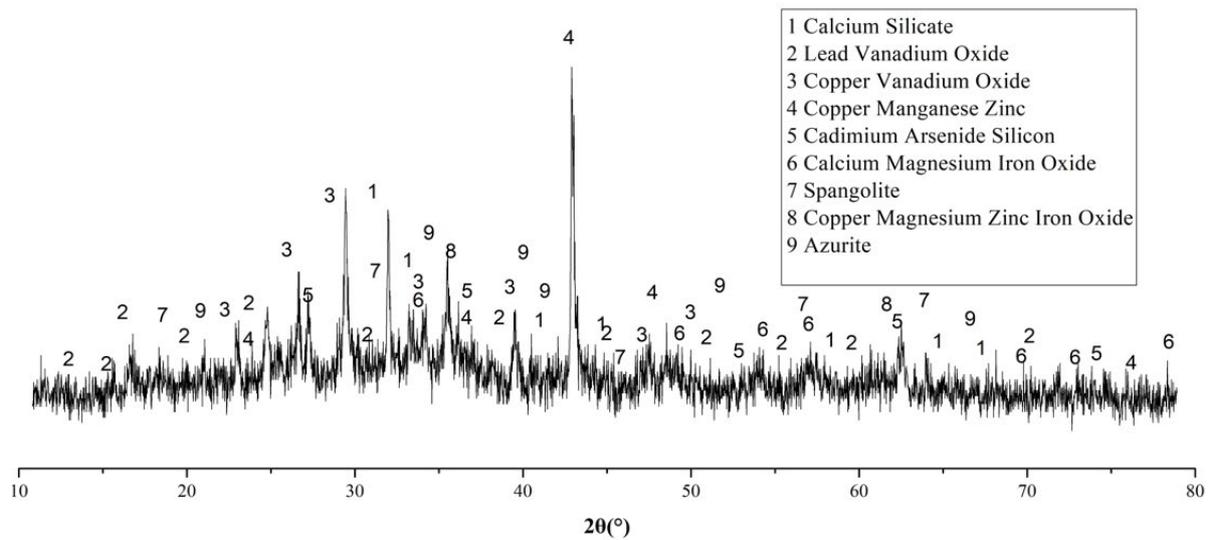


Fig. 8. XRD pattern of Cu(II), (b) Cd(II), (c) Pb(II), and Zn(II) co-adsorption onto BOFs.

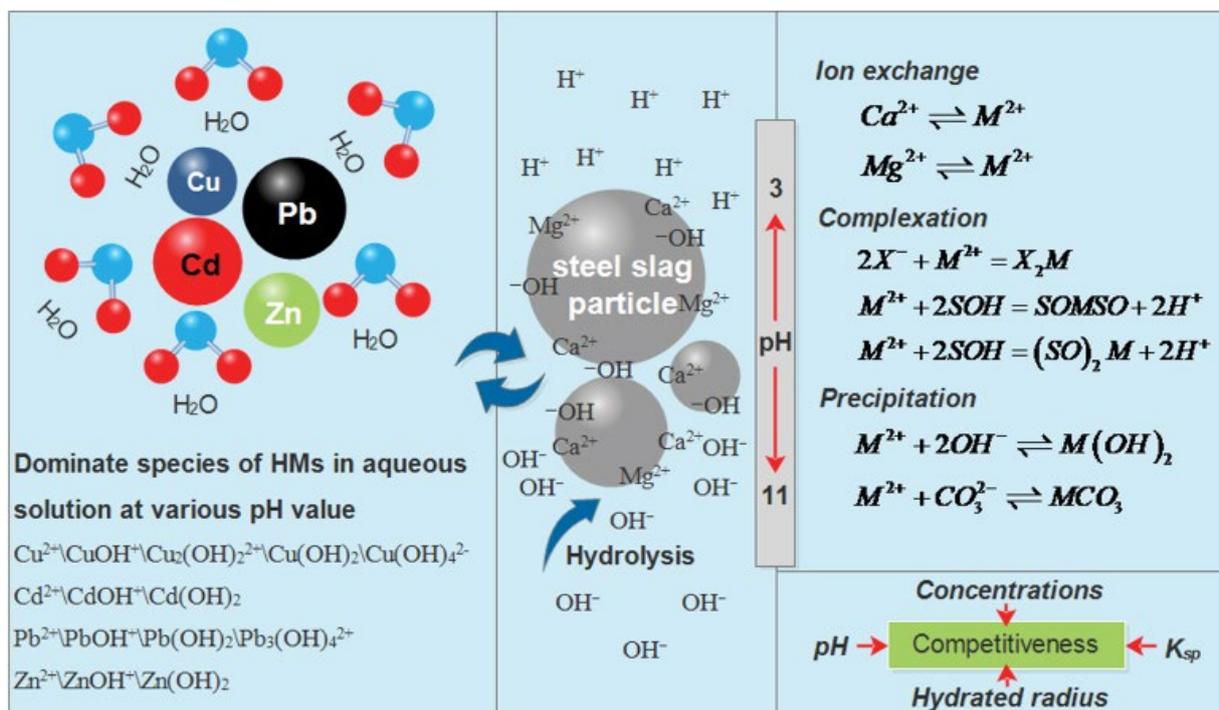


Fig. 9. Possible reaction path and mechanism.

factors [25,34]. Due to the complex composition of BOFs, it was not clear to demonstrate the mechanism of co-adsorption heavy metals onto BOFs by using the XRD, which means more details would be necessary.

### 3.3.2. Possible reaction path of heavy metals by BOFs

Many researches have been reported to interpret the adsorption mechanism of heavy metals onto BOFs [19,25]. The effect of ion exchange and precipitation or co-precipitation was usually used to describe the adsorption reaction. This work provided a possible reaction path of co-adsorption of four kinds of heavy metals onto BOFs in Fig. 9. Wide pH range was set and different heavy metals dominate species was shown in aqueous solutions with various pH values. Then the BOFs hydrolyzed in solution accompany with occurring the reaction of ion exchange, surface complexation and chemical precipitation between heavy metals with BOFs. For the competitive adsorption process, four main factors were considered to influence the adsorption capacity. First, the ratios of metal ions substituted by other competitive metal ions in multi-metal adsorption remain consistent over a wide range of metal concentrations. Then, the pH value of the solution significantly influenced the products after the reaction. Even the solidity ( $K_{sp}$ ) would lead to different products after reaction in the competitive system. Finally, the effect of the hydrated radius of heavy metal on adsorption capacity was significant. Usually, the smaller the ionic radius of hydration is, the stronger the ion exchange capacity is. However, the co-adsorption onto BOFs is a kind of more complicated reaction, which means it is not possible to determine the adsorption mechanism by emphasizing any of factor from above. It depends on the combined effects

of all factors. The weight of any factor needs to be carefully discussed. Besides, BOFs can be used as alkali adsorbent to precipitation heavy metals when used in acidic wastewater treatment. The strong acid-neutralizing capacity of BOFs assured the better removal rate of heavy metals from acid wastewater, even some chemical compounds were not stable.

## 4. Conclusion

Single and multi-metal adsorption of heavy metals in BOFs was investigated to estimate the adsorption behavior of heavy metals in this work. The fineness of BOF particles modified by the effect of mechanochemistry significantly influenced the maximum capacity. The adsorption equilibrium time was close to 180 min while the maximum adsorption capacity was higher than 390 mg L<sup>-1</sup>. Increasing the initial concentration of adsorbates would lead to an increase in adsorption capacities. The highest adsorption capacity was beyond 510 mg L<sup>-1</sup>. The removal efficiency increased with an increase in pH value. Particularly in an acid solution, the higher removal efficiency for each heavy metal was obtained. Increasing the temperature was in favor of adsorption reaction and increased the maximum adsorption capacity of each metal onto BOFs. For the single adsorption system, the Freundlich model was well-fitted than Langmuir in the description of adsorption isotherm while the pseudo-second-order model was closer to experimental results.

In binary adsorption system, the equilibrium adsorption capacity of coexisting heavy metals Cd(II), Pb(II), and Zn(II) was almost invariably with an increase of initial concentration of Cu(II) in Cu-Cd, Cu-Pb, and Cu-Zn mixed solutions.

Cu(II) showed the weak adsorption competitiveness of Cu(II) in the ternary system while the heavy metal competitive adsorption order was Pb(II)>Cd(II)>Zn(II)>Cu(II) in fourfold system. XRD analysis was consistent with the published report and it was not clear to demonstrate the mechanism of co-adsorption heavy metals onto BOFs due to lack of key information. The possible reaction path provided by this work emphasized the four factors which mainly influenced the co-adsorption reaction. Besides the concentration of heavy metals and pH of the solution, the hydrated radius of heavy metal ion and co-efficient of the solidity of products formed in the process of precipitation were contributing to the adsorption competitiveness of heavy metals.

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