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STUDY OF THE ADSORPTION OF Cu²⁺, Cd²⁺ AND Pb²⁺ ON AMORPHOUS AI(OH)₃ IN DRINKING WATER SUPPLY NETWORKS

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Abstract

Trace metal elements commonly exist in drinking water. Excessive exposing on them may result in lots of health problems. This paper mainly focuses on the accumulations of Cu^{2+} , Cd^{2+} , and Pb^{2+} in drinking water supply networks with amorphous Al(OH)₃ formation. The effects of pH, water flow rate, and metal element contents were investigated at laboratory bench scale. It was found that chemical adsorption mainly occurred at pH > 7.0. Suspended Al(OH)₃ showed a strong adsorption capacity for Cu²⁺, Cd²⁺, and Pb²⁺; 1.0 g Al(OH)₃ could accumulate 43.0 mg of Cu²⁺, 30.0 mg of Cd²⁺, and 34.6 mg of Pb²⁺ at 15°C, respectively. Thermodynamic calculation results indicated nearly all of the Cu²⁺ and Cd²⁺ were adsorbed at pH 6.5-8.5, chemical precipitation did not occur in the presence of suspended Al(OH)₃. Because of H⁺ inhibition, the adsorption of Cu²⁺, Cd²⁺, and Pb²⁺ would be inhibited under acidic condition. Unlike suspended Al(OH)₃, Al(OH)₃ scale showed a much lower adsorption capacity for Cu²⁺, Cd²⁺, and Pb²⁺, at approximately 0.4, 0.4, and 0.7 mg/g, respectively; and the variation of flow velocity and solution pH had minor effects.

Key words: aluminum hydroxide, drinking water, pipe scale, water quality

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1. Introduction

Trace metal elements commonly exist in drinking water. Excessive exposure to copper, cadmium, and lead will result in serious health problems via bioaccumulation in living tissues (Jamali et al., 2014; Piyaratana et al., 2008). In addition, the accumulation of copper or lead containing sediments can lead to a reduction in water pressure and flow transport capacity in the pipes (USEPA, 2008). Most of the Cu²⁺, Cd²⁺, and Pb²⁺ enter water supply networks from the corrosion of

plumbing materials (USEPA, 1995) or leaching from cement linings. Incidents of cross-connection can also release toxic amounts of metal elements into drinking water (USEPA, 2002). It should be noted that consumers do not drink water directly from the source or immediately after treatment but rather water that has traveled through supply networks (Schock, 2005). However, the concentrations of trace metal elements in the tap water may vary notably as the adsorption-desorption and precipitationdissolution processes occur within the pipeline. Polyaluminum chloride is commonly used in water

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treatment plants (Wang et al., 2010). As its solubility is relatively low, aluminum containing sediments usually formed in the pipe line (Snoeyink et al., 2003; Swaddle, 2001). Many studies have found that the amorphous $Al(OH)_3$ formed in coagulation exhibits a good adsorption capacity to many metal elements (Goldberg et al., 1996; Schock and Holm, 2003). Sudden reductions in lead levels are observed during the pipe rig testing, which is coincided with the deposition of $Al(OH)_3$ on the lead pipe (Kirmeyer et al., 1999).

In a public building with no lead pumbing in Wales, high concentrations of lead and copper are observed in the drinking water. Further investigation indicates that the copper pipe is heavily covered with aluminum containing scale (Fuge and Perkins, 1991). Unpredictable short term elevations of metal concentrations will result if the water quality changes (Schock and Holm, 2003; USEPA, 2006). It has been demonstrated that the mechanism of metal ions association with hydrous oxide surfaces involves an ion exchange process in which the adsorbed metal ions replace bound protons (Schindler, 1981; Tsekova et al., 2015). The adsorption of Cu^{2+} and VO_2^+ on aluminum hydroxide is considered to be a chemical process. Chisholm-Brause et al. (1990) studies the adsorption of Pb^{2+} on γ -A1₂O₃ using a combination of XANES and EXAFS spectroscopies and concludes that inner-sphere, predominantly monodentate complexes are formed. Benjamin and Leckie (1980) find that Zn2+ and Cd2+ will compete for the same group of binding sites, whereas Cu²⁺ and Pb²⁺ bind preferentially to other groups of sites. However, most of the experimental results are obtained in systems using γ -Al₂O₃ or aluminum hydroxide crystals as adsorbents, the accumulation characteristics of trace metal elements on amorphous Al(OH)₃ solids formed in drinking water supply networks are still not clear. Many drinking water purification plants in China are currently considering disinfection byproduct precursors, removing changing water sources and coagulant type, or the combination of these measures to make sure the treated water quality meeting the new standard (GB5749-2006). These changes can affect the occurrence, chemical and physical characteristics, and the stability of aluminum hydroxide solids attached on the inner pipe surfaces, and thus affects their accumulation for trace metal elements. The objective of this paper is to (1) study the adsorption of Cu²⁺, Cd²⁺, and Pb²⁺ in water supply networks with Al(OH)₃ formation; (2) investigate the effects of solution pH, water flow rate, and metal element contents on the adsorption process; and (3) reveal the adsorption characteristics of Cu^{2+} , Cd^{2+} , and Pb^{2+} on amorphous Al(OH)₃.

2. Experimental materials and methods

2.1. Sorption test on Al(OH)₃ scale

Experiments were conducted in a water supply modeling system (Fig. 1). Pipe water was prepared from deionized water by adding certain amounts of 0.50 mol/L NaOH, 0.50 mg/L HNO₃, 100 mg/L Al₂(SO₄)₃, and 50.0 mg/L Cd(NO₃)₂, Cu(NO₃)₂, and Pb(NO₃)₂ into the tank in which a stirring device was fixed to guaranty complete mixing. The synthetic water was pumped into the pipe system using a constant flow pump (BT-102, Zhisun Instrument, China).

To exclude the affection of pipe corrosion on the concentrations of trace metal elements, polyvinyl chloride pipes were used in the system. The pipe water quality was controlled in the range of actual drinking water distribution systems. Reagent grade chemicals were used except where noted. Water temperature was controlled at 15° C by putting the tank to an incubator (SPX-250B, Tianjin Taisite Instrument, China).

To accelerate the formation of $Al(OH)_3$ scale, the initial solution pH and aluminum concentration of the solution was maintained at 6.5 and 50.0 mg/L, respectively. After 5 days of operation, a white gelatinous pipe coating mainly composed of $Al(OH)_3$ was generated. Next, the $Al_2(SO_4)_3$ addition was removed and 1.0 mg/L target metals was introduced to the system to observe the adsorption characteristics of $Al(OH)_3$ for trace metal elements in stage I.

In stage I, solution pH and temperature were maintained at 7.5 and 15°C, respectively. To insure that the added metal elements were fully mixed with the Al(OH)₃ scale, its flow velocity was maintained at 0.5 mL/s, much lower than the normal rates observed in distribution systems. When the concentrations of metal elements in the effluent was stable, the effects of solution pH, water flow rate and total metal element inputs on adsorption were investigated at stage II (Table 1). Water samples were taken at different time intervals and filtered through a 0.45 μ m polycarbonate membrane for further analysis.



Fig. 1. Water supply modeling system used in the experiment

Adsorbates	Factors	Units	Stage I	Stage II		
			Mid-level	Low level	High level	
Cd^{2+}	pН	-	7.5	6.50	8.50	
	Cd^{2+}	mg/L	1.17	0.00	1.45	
	v	mL/s	0.5	0.2	1.0	
Cu ²⁺	pН	-	7.5	6.50	8.50	
	Cu ²⁺	mg/L	1.1	0.00	1.90	
	v	mL/s	0.5	0.2	1.0	
Pb ²⁺	pН	-	7.5	6.50	8.50	
	Pb ²⁺	mg/L	0.83	0.00	1.60	

mL/s

0.5

Table 1. Effecting factors and levels selected in stages I and II

2.2. Sorption test in $Al(OH)_3$ suspension

Batch adsorption experiment was examined to determine the sorption capacity of suspended Al(OH)₃ for Cu²⁺, Cd²⁺, and Pb²⁺. 0.20 g of air-dried Al(OH)₃ was placed into 250 mL tubes which were stirred using a magnetic stirrer (JZG9-S-6A, Xihuayi Technology Corporation, China). Then, 25.0 mg/L $Cu(NO_3)_2$, $Cd(NO_3)_2$, and $Pb(NO_3)_2$ were added after 0.0, 6.0, and 14.0 min of adsorption to maintain the total metal element inputs at 0.1, 0.5, and 1.0 mg/L, respectively. The mixtures were sampled before and immediately after the increase of adsorbate contents and centrifuged at 5000 rpm for 20 min. The sorption coefficients (K_d) were calculated as the ratio of the amount of metals adsorbed on Al(OH)3 and the amount of metal residual in the water at equilibrium, as shown in Eqs. (1).

v

$$=AlOH^{0.5-} + M^{2+} \to =AlOM^{0.5+} + H^{+}$$
(1)

where =AlOH^{0.5-} and =AlOM^{0.5+} are the active adsorption site on the amorphous Al(OH)3 solid before and after adsorption for metal elements. All the water quality parameters were maintained in the range of actual drinking water (Table 1). The formation of surface complexes was conceptualized similarly to what was measured in solution. The amounts of trace metal elements adsorbed by suspended Al(OH)₃ were predicted applying the Visual Minteg software. By defining the type of the adsorption surfaces (1), adsorption model (diffused layer model), solid concentration (0.05 mg/L), site concentration (1.0 mmol/mmol solid), and the sorption coefficient (K_d), the reactions between Cd^{2+} , Cu^{2+} , and Pb^{2+} and suspended Al(OH)₃ were predicted (Pommerenk and Schafran, 2005).

2.3. Water quality and solid analysis methods

The concentrations of aluminum, calcium, magnesium, iron, cadmium, copper, and lead were determined using an ICP-AES (IRIS intrepid- II, Thermo Scientific, USA). Sample aliquots were acidified with trace metal grade nitric acid to pH < 2.0 for 12 h before analysis. Solution pH was determined using a pH meter (Model 828, Thermo Electron Corporation, USA); water temperature was determined with a thermometer (Model TTM1-JM-

6200IM, Yuan-Da Technology Corporation, China). All the parameters were analyzed according to the standard methods described in GB/T 5750.4-2006 of China.

1.0

0.2

To observe the surface characteristics of $Al(OH)_3$ solid, scanning electron microscopy combined with an energy dispersive spectrometer (SEM/EDS) (JSM-6490LV, JEOL Ltd., Japan) and a X ray diffractometer (Ultima IV, Rigaku Corporation, Japan) were applied. The SEM/EDS samples were sputter-coated with gold before conducting surface scanning. Specific area was measured using a Micromeritic Gemini model VII 2390 and an adsorption volumetric system with a pressure transductor (MKS Baratron 170 M).

3. Results and discussion

3.1. Cu^{2+} , Cd^{2+} , and Pb^{2+} adsorption on $Al(OH)_3$ scale

Experiments were conducted with flow velocity, solution pH, and total metal element inputs maintained at approximately 0.5 mL/s, 7.5, and 1.0 mg/L respectively in stage I. Initially, the concentrations of residual Cu²⁺, Cd²⁺, and Pb²⁺ were the lowest in the effluent, at approximately 0.61, 1.06, and 0.25 mg/L, respectively (Fig. 2). However, thermodynamic calculation results showed that more than 50% of the Cu²⁺ and 90% of the Pb²⁺ would precipitate in the forms of $Cu(OH)_2$ and $Pb(OH)_2$ in solutions without Al(OH)₃ formation, both lower than the determined values. When the flow volume was above 0.6 L, the concentrations of residual Cu^{2+} , Cd²⁺, and Pb²⁺ reached stability. Compared with Cu²⁺ and Pb²⁺, little Cd²⁺ was removed close to the input value at the end of stage I. Al(OH)₃ reached its maximum adsorption capacity.

The amounts of Cu^{2+} , Cd^{2+} , and Pb^{2+} adsorbed by deposited Al(OH)₃ were approximately 0.41, 0.40, and 0.72 mg/g, respectively. To investigate the effects of solution pH, water flow velocity, and total metal element inputs on Al(OH)₃ adsorption, the system was operated under different conditions in stage II. When the addition of Cu^{2+} , Cd^{2+} , and Pb^{2+} were stopped, all of them were not detected in the effluent, indicating that the adsorption of trace metal elements on Al(OH)₃ scale was strong.



Fig. 2. Effects of flow velocity (v), solution pH (pH), and total metal element inputs (C) on the concentrations of residual Cu^{2+} , Cd^{2+} , and Pb^{2+}

However, as Al(OH)₃ scale reached its maximum adsorption capacity, the total inputs of Cu^{2+} , Cd^{2+} , and Pb^{2+} increased to high levels, suggesting they could not be removed further.

Increasing solution pH from 7.5 to 8.5, both Cu^{2+} and Cd^{2+} suddenly released in the exchanging process. Concentrations of them decreased gradually to the values before pH adjusted (Fig. 2). Although the solubility of Cu^{2+} and Pb^{2+} was low at pH 8.5, most of the Cu and Pb were not removed because of the effects of reaction kinetics, around 0.78 and 0.35 mg/L. Unlike the case at pH 8.5, the concentrations of residual Cu^{2+} and Pb^{2+} were higher than the amounts added, indicating that part of the removed Cu^{2+} and Pb^{2+} was also released to the solution at pH 6.5, and that the combination between amorphous Al(OH)₃ and metal cations was weakened under the acidic condition (Fonseca et al., 2006).

When the flow velocity was 1.0 mL/s, portions of the adsorbed Cu^{2+} , Cd^{2+} , and Pb^{2+} were flushed into the water, and thus led to their concentrations suddenly increasing in the effluent (Fig. 2). However, when the flow velocity decreased to 0.2 mL/s, more Cu^{2+} and Cd^{2+} were removed suggesting removal from the precipitation of suspended particles. In drinking water distribution systems, however, amorphous Al(OH)₃ usually

formed with the adsorption of pollutants simultaneously; metal elements not only existed on the surface but also inside of Al(OH)₃ scale. To simulate the adsorption occurring during the formation process of deposited amorphous Al(OH)₃, static experiments were also conducted.

3.2. Cu^{2+} , Cd^{2+} , and Pb^{2+} adsorption on suspended $Al(OH)_3$

When the solution pH was above 7.5, all of the Cu²⁺ and Pb²⁺ inputs were removed, which might contribute to the adsorption of suspended Al(OH)₃ and chemical precipitation in the forms of Cu(OH)₂ and Pb(OH)₂. While according to the speciation of copper, cadmium, and lead under the same water quality calculated applying the Visual MINTEQ software, Cu(OH)₂ and Pb(OH)₂ precipitation would not form in the system. Besides, from the X-ray diffraction spectrum of the solids after adsorption, it was also difficult to observe the peaks contributed by Cu(OH)₂, Pb(OH)₂, and other crystals (Fig. 3). Cai and Braids (2001) also found that the adsorption of Pb²⁺ on the soil solids increased sharply with solution pH. Accordingly, the removal of Cu^{2+} and Pb^{2+} was likely a result of the adsorption process. The concentrations of residual Cu²⁺, Cd²⁺, and Pb²⁺ were

stable with reaction time at pH 6.5, while the increase of their total input would lead to a notable increase in the effluents (Fig. 4). Hachiya et al. (1979) found that the adsorption and desorption reactions of Pb²⁺ on γ -A1₂O₃ was very fast, with half-times less than 1 s under typical experimental conditions. When the total metal elements addition was 0.5 mg/L, the concentrations of residual Cu2+ and Cd2+ were 0.05 and 0.29 mg/L; while Pb²⁺ was not detected (Fig. 4). In solutions with 1.0 mg/L Cu²⁺, Cd²⁺, and Pb²⁺ addition, their residual concentrations increased notably to 0.09, 0.61, and 0.17 mg/L respectively. Further supporting that most of the Cu²⁺ and Pb²⁺ were mainly adsorbed by Al(OH)₃. On the basis of the concentrations of total and residual Cu²⁺, Cd²⁺, and Pb^{2+} , the adsorption constants (K_d) of Cu²⁺, Cd²⁺, and Pb²⁺ were calculated (Table 2). The specific surface area and surface site density of amorphous Al(OH)₃ were assumed to be constant at 900 m^2/g and 1.0 mmol/mmol, respectively (Pommerenk and Schafran, 2005). Applying diffuse layer adsorption model, residual Cu²⁺, Cd²⁺, and Pb²⁺ concentrations were predicted (Fig. 5).

Calculations indicated that the concentrations of Cu²⁺ and Pb²⁺ removed from drinking water were close to the predicted values at pH > 6.5, which was mainly contributed by a chemical adsorption process (Schindler, 1981). Similar experimental result was obtained at pHs below 7.0 for Cd²⁺ adsorption. Mcbride (1982) also found nearly all of the Cu²⁺ addition could be adsorbed by noncrystalline alumina, boehmite, and gibbsite at pHs above 6.5. At pH < 6.5, however, the concentrations of Cu²⁺ and Pb²⁺ being removed were higher than the predicted values.

From Eq. 1, it suggested that the adsorption of metal elements on amorphous Al(OH)₃ was pH dependent. The combination of M^{2+} with =AlOH^{0.5-} would be inhibited in solutions with more H⁺. As shown in Fig. 5, the concentrations of residual metal elements were higher in acidic conditions. However, they were much lower than the calculated values, indicating in addition to the combination of M²⁺ with =AlOH^{0.5}, physical adsorption must also contributed to removal of Cu²⁺, Cd²⁺, and Pb²⁺ (Jusoh et al., 2005). Chisholm-Brause et al. (1990) also found similar experimental results when studying the adsorption of γ -A1₂O₃ for Pb²⁺. The adsorption characteristics of amorphous Al(OH)3 made with high pollutants removing capacity in drinking water pH range. However, as the combination strength caused by physical adsorption was usually weaker than that of chemical adsorption, flow velocity and drinking water quality might lead to a suddenly desorption of Cu2+, Cd2+, and Pb2+, which was supported by the experimental results obtained under acidic conditions in section 3.1.

EDS analysis results showed that aluminum and oxygen were the major elements (Table 3). The Al/O molar ratio was approximately 1:3, which corresponded well with the elements composition of amorphous Al(OH)₃. Copper, cadmium, and lead were not detected; while after adsorption, their molecular weight ratios were approximately 1.3%, 0.6%, and 0.3% respectively. 1.0 g of suspended Al(OH)₃ could adsorb 43.8 mg of Cu²⁺, 30.0 mg of Cd²⁺, and 34.6 mg of Pb²⁺, much higher than the value adsorbed by Al(OH)₃ scale.



Fig. 3. XRD spectrums of Al(OH)₃ scale (1) and suspended Al(OH)₃ adsorbed with Cu²⁺ (2), Cd²⁺ (3), and Pb²⁺(4)



Fig. 4. Adsorption of Cu^{2+} , Cd^{2+} , and Pb^{2+} on amorphous Al(OH)₃ suspension



Fig. 5. Residual concentrations of Cu²⁺, Cd²⁺, and Pb²⁺ at different solution pH

This response might be related to their structure characteristics.

Metal elements	=AlOH ^{0.5-} (μmol)	Total M ²⁺ (µmol)	M ²⁺ (μmol)	=AlOM ^{0.5+} (µmol)	H⁺ (µmol)	LogK _d	$\overline{LogK_d}$
Cu ²⁺	633	8.0	0.16	7.66	0.316	-1.61	-1.85
	626	15.0	0.63	15.00	0.316	-1.92	
	611	31.0	1.25	30.00	0.316	-1.91	
	596	46.0	2.28	44.59	0.316	-1.98	
Cd^{2+}	641	4.5	4.03	0.43	0.316	-4.28	-4.39
	640	9.0	8.34	0.59	0.316	-4.46	
	640	18.0	16.70	1.16	0.316	-4.46	
	639	26.5	24.59	2.20	0.316	-4.35	
Pb ²⁺	639	2.4	0.07	2.34	0.316	-1.80	-2.28
	637	4.8	0.39	4.44	0.316	-2.24	
	632	9.6	0.97	8.70	0.316	-2.35	
	630	14.5	3.18	11.31	0.316	-2.75	

Table 2. Adsorption constants between amorphous Al(OH)₃ and Cu²⁺, Cd²⁺, and Pb²⁺ at 15 °C

Table 3. Elements composition of amorphous Al(OH)3 before (a) and after (b) adsorption

Elment	Patona adaption (mala 9/)	After adsorption (mole %)			
	Before ausorption (mole %)	<i>Cu</i> ²⁺	Cd^{2+}	<i>Pb</i> ²⁺	
0	74.33	74.51	74.31	76.15	
Al	23.54	23.00	22.12	21.47	
S	2.12	1.11	2.55	2.09	
Cu	-	1.25	-	-	
Cd	-	-	0.46	-	
Pb	-	-	-	0.28	



Fig. 6. SEM pictures of amorphous Al(OH)3 scale (a) and suspension Al(OH)3 (b).

Although the XRD spectrums of deposited and suspended Al(OH)₃ solids were similar (Fig. 3). Both in an amorphous state and the specific surface area of the deposited Al(OH)₃ was about 160 m²/g, much lower than that of suspended Al(OH)₃. The differences in specific area could also be observed from their SEM pictures as shown in Fig. 6, further supporting suspended Al(OH)₃ had a stronger adsorption capacity for trace metal elements.

4. Conclusions

The adsorption of trace metal elements on amorphous Al(OH)₃ scale is a complex process. In the formation of Al(OH)₃ scale, its adsorption capacity was high; 1.0 g solid could accumulate 43.0 mg of Cu²⁺, 30.0 mg of Cd²⁺, and 34.6 mg of Pb²⁺. Thermodynamic calculation results showed that they were mainly removed by the adsorption of amorphous Al(OH)₃. Chemical adsorption mainly took place at pH > 7.0; In drinking water with pH < 6.5, the adsorption of Cu²⁺, Cd²⁺, and Pb²⁺ on amorphous Al(OH)₃ would be greatly inhibited. The adsorption characteristics of amorphous Al(OH)₃ solid indicated a high metal pollutant removing capacity in the pH range of general drinking waters.

When Al(OH)₃ formation was halted due to variations in the water quality, its adsorption capacity for Cu²⁺, Cd²⁺, and Pb²⁺ would decrease drastically to approximately 0.41, 0.40, and 0.72 mg/g, respectively. However, the combination between trace metal elements and amorphous Al(OH)₃ was also strong at pH 7.5. When our system stopped the metal elements addition, the Cu²⁺, Cd²⁺, and Pb²⁺ were no longer detected in the effluent. Considering the effects of solution pH and water flow velocity on the adsorption of Cd²⁺, Cu²⁺, and Pb²⁺, better management of water age and sediment accumulation was suggested to control the concentration of trace metal elements in the tap water.

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