

Removal of Lead(II) and Copper(II) from Hypersaline Media With Amorphous Tin(IV) Phosphate

WEN-BIN CHEN^{1,*} and ZHEN CAO²

¹Department of Chemical Engineering, Huaihai Institute of Technology, Lianyungang 222005, Jiangsu Province, P.R. China

²School of Chemistry Engineering, Huaihai Institute of Technology, Liangyungang 222005, Jiangsu Province, P.R. China

*Corresponding author: Tel: +91 13912168711; E-mail: lygcswb11@163.com

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Amorphous tin(IV) phosphate was used as adsorbent for the removal of Pb(II) and Cu(II) from aqueous solutions. The extent of absorption was investigated as a function of pH, contact time, adsorbent concentration and ionic strength. Experimental results showed that the amount of adsorbed heavy metal ions increased with the increase of solution pH in the examined range (3.0-6.5) and reaction time. The equilibrium data were analyzed using the Freundlich and Langmuir isotherm models. The results showed that the sorption process followed Langmuir model well. The maximum sorption capacity amounted to 378.79 and 250.0 mg/g at 25 °C for Pb(II) and Cu(II), respectively. The free energy E_s (kJ/mol) got from the Dubinin-Radushkevich isotherm indicated the sorption processes are chemical ion-exchange mechanism. The sorption mechanism of the process is the ion-exchange reaction between heavy metal ions and H^+ . The negative ΔG° values confirm the adsorption processes are spontaneous. Ionic strength experiments show that it is feasible for amorphous tin(IV) phosphate in removing Pb(II) and Cu(II) from marine culture wastewater, though hyper-saline media has a certain harmful effect.

Key Words: Amorphous tin(IV) phosphate, Hypersaline media, Lead, Copper, Ion exchange.

INTRODUCTION

With the rapid development of economy, the problem of environmental pollution has become increasingly worse, more and more sea shores are polluted by heavy metals in varying degrees. As a result of heavy metal ions are characterized by their extensive distribution, long duration and have the character of hard to decomposition in the material circulation and energy exchange, so they can concentrate in organisms and be transferred by food chain, then finally affect human health.

Chen *et al.*¹ had researched the content and distribution characteristics of the heavy metal ions in the offshore sea water, sediment and shellfish. They found that there were six heavy metal ions (Hg, As, Cu, Pb, Cd and Zn) in seven organisms in about 36 samples and were out of limit in varying degrees.

Wang *et al.*² found that *Mactra veneriformis* had a strong resistance properties of Cd^{2+} and Hg^{2+} and easy to concentrate, while not easy to show the intimidated symptoms. Kumaqai and Sacki³ found that content of Hg, Cd, Pb and As increased with the growth of the body length while determined heavy metals in Japan Tapes literatures.

Among the methods of removing heavy metals, absorption method especially suitable for disposing heavy metal wastewater in low concentration with its less investment, simple operation and wide applicability, *etc.* However, absorption performance of most adsorbent declined rapidly with the

increase of the ionic strength⁴, so it is inapplicable in hypersaline seawater.

Tin(IV) phosphate insoluble in water and organic solvents has other characteristics, such as it can resistant to strong acidity and a certain of alkalinity and resistant to radiation, has strong thermal stability and mechanical strength and high chemical stability, high specific surface area and larger surface charge density, *etc.* In this study, we have investigated the dynamics and thermodynamics rule and salinity effect on absorption performance of amorphous tin(IV) phosphate adsorbed Pb(II) and Cu(II), which obtained through chemical synthesis. So we can use it to provide the theory basis and the technical guidance for developing and utilizing Amorphous tin(IV) phosphate to remove metal ions in marine culture wastewater.

EXPERIMENTAL

Electronic balance (BS224S, Beijing Sartorius balance Co., Ltd.); Precision pH meter (PHSJ-5, Shanghai Leici company); intelligent temperature air oscillator (HZQ-QX, Harbin DongLian electronic technology development Co., Ltd.); potentiometric titrator (ZDJ-4 A, Shanghai precision & Scientific instrument Co., Ltd.); atomic absorption spectrophotometer (TAS-990, Beijing general chromatography general instrument Co., Ltd.); X-ray diffractometer (X, TRA, Switzerland ARL company). Regents used in the experiment were analytically pure.

Material preparation: The amorphous tin(IV) phosphate was prepared according to the reported method⁵. The 0.3 mol/L SnCl₄ was added to 0.6 mol/L H₃PO₄ solution dropwise at room temperature and stirred continuously, after totally reacted, ageing for the overnight. Keep washing the product with distilled water until there was no Cl⁻ detected, and preserved it in dryer after vacuum drying (45 °C), polished and milled in 160 mesh screen.

The XRD figure of the sample (Fig. 1), showed the diffraction peak of tin(IV) phosphate which in the position near a 2θ for 21°, 26°, indicating that the product was amorphous tin(IV) phosphate.

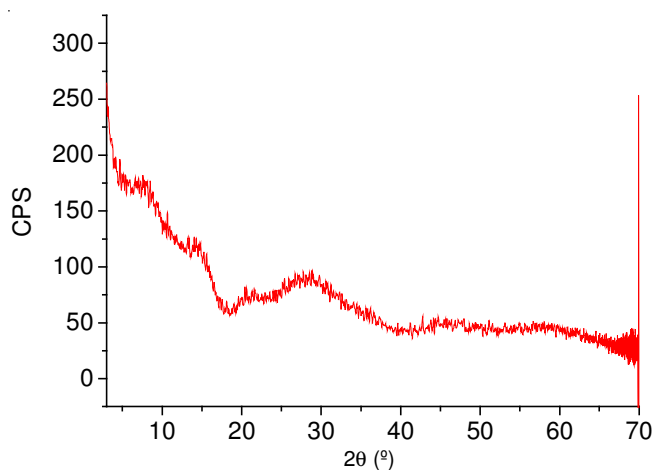


Fig. 1. XRD spectrum of amorphous tin(IV)-phosphate

Absorption balance experiment: Took a certain quality of the sample in 250 mL tapered bottle, joined a certain volume of Pb²⁺ (or Cu²⁺) reserved liquid, added distilled water to 50 mL, then obtain the solution of required concentration, with 0.5 mol/L NaOH or HNO₃ to adjust solution pH value, then oscillated at certain temperature in constant temperature oscillator (120 r/min). Take out the sample when it reached the reaction time, filtered, abandoned the initial 30 mL filtrate and determined the metal ions content of remaining filtrate by flame atomic absorption spectrometry.

Calculated the adsorption q (mg/g) as the following equation:

$$q = \frac{(C_0 - C_e)V}{m}$$

In the equation: C_0 is the initial mass concentration of metal ions, mg/L; C_e is the balance concentration of metal ions, mg/L; V is the volume of solution, L; M is the sample quality, g.

Analysis method of Pb²⁺ and Cu²⁺: Concentration of Pb²⁺ and Cu²⁺ were analyzed by atomic absorption spectrophotometry (GB/T 7475-1987).

RESULTS AND DISCUSSION

Influence of pH: A number of 50 mL metal ionic solution (50 mg/L) to the volumetric flask (250 mL), separately adjusted to different pH value, added 0.1 g sample, oscillated for 24 h at 25 °C and filtered, measured the concentration (Fig. 2).

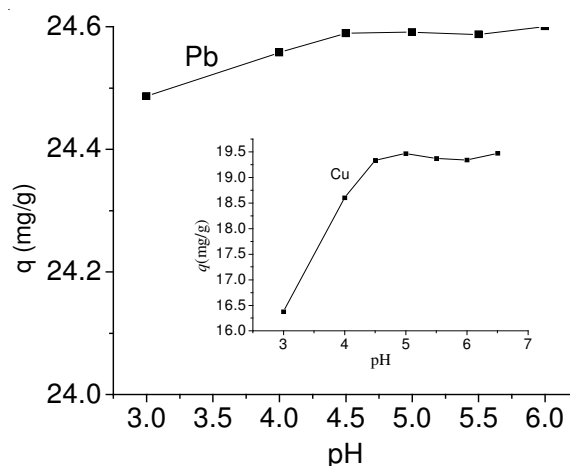


Fig. 2. Effect of pH on the sorption of Pb(II) and Cu(II) with amorphous tin(IV) phosphate

The pH value has an effect on the absorbent surface charge and ionization degree, so it is an important factor in the absorption process. Fig. 2 showed that the absorption capacity of Pb²⁺ and Cu²⁺ to amorphous tin(IV) phosphate increased rapidly with the rising of pH value in the range of 3.0-4.5. The absorption capacity stabilized basically when the pH > 5. This might be that when the pH value was low, the H⁺ ions in the solution were more and around the absorbent, repulsed to the positive charge metal ions, influenced the absorption of absorbent to metal ions⁶. When the pH value arose to 4.5, the absorption and desorption of amorphous tin(IV) phosphate's surface adsorption location achieved a dynamic equilibrium. It could also because it formed a soluble and hydroxo complex. That was not benefit to the reaction, made the adsorption increased no longer⁷. In the subsequent experiment, the pH value was 5.

Influence of time on adsorption process: Accurately transferred 50 mL of 50 mg/L metal ions standard solution into a series of tapered bottles, adjusted pH value to 5.00 ± 0.02, added 0.1 g sample, respectively, oscillated in different time at 25 °C, respectively then filtered, determined the concentration of the metal ions in the filtered solution (Fig. 3).

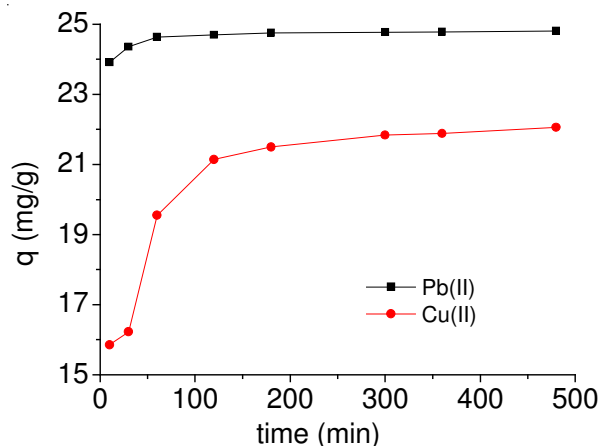


Fig. 3. Effect of time on the removal of Pb²⁺ and Cu²⁺ (25 °C)

From Fig. 3, we could find out that, the absorption capacity of Pb²⁺ and Cu²⁺ to amorphous tin(IV) phosphate showed a

rising trend as time past. Its absorption process might be divided into two phases, fast absorption phase (Pb^{2+} : before 1 h, Cu^{2+} : before 2 h) and gradually stable equilibrium phase. This was because in the start phase of the absorption, there were enough absorption sites on the surface of absorbent, then the absorption capacity increased rapidly and the absorption sites became less and less⁸ as metal ion's coverage was bigger and bigger, absorption of Pb^{2+} and Cu^{2+} achieved basic balance, respectively at 6 and 8 h.

Li *et al.*⁹ showed that the absorbed Pb^{2+} in the solution with abandoned wheat berry at the temperature of 10, 20, 30, 40 °C, they all reached absorption balance after 0.5 h and the absorption capacity was in 3.4 mg/g or so. Benhammou *et al.*¹⁰ used humite to adsorb Cu^{2+} , its balance time was 1 h and the absorption capacity was 10.56 mg/g. Its absorption rate was faster than our experiment, but the experimental absorption effect was better, absorption capacity of Pb^{2+} was about 24.5 mg/g, absorption capacity of Cu^{2+} was about 22 mg/g.

Study of isothermal absorption: Accurately transferred 50 mL of standard solution of metal ion in different initial concentration, respectively and set the pH value to 5.00 ± 0.02 , respectively cast 0.1000 g sample, oscillated at 25 °C, filtered after the balance, determined the metal ionic concentration of the filtrate (Fig. 4).

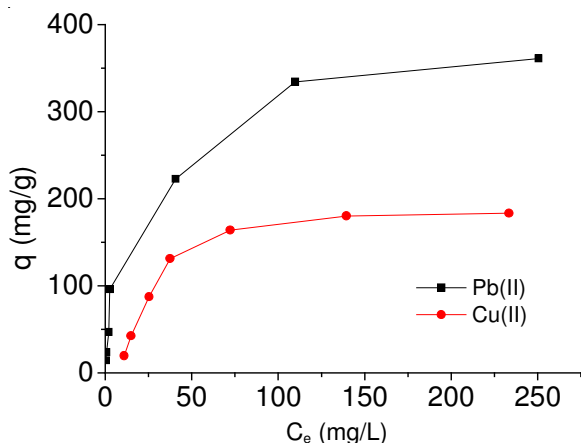


Fig. 4. Sorption isotherm of Pb^{2+} and Cu^{2+} on amorphous tin(IV) phosphate

The best method is to evaluate the absorption ability of absorbent was using isotherm to describe the whole absorption process. This paper used Langmuir model, Freundlich model, Dubinin-Radushkevich model to fit.

Langmuir model

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (1)$$

Usually described in linear expression:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{1}{q_m} C_e \quad (2)$$

In formula: q_m is the biggest metal ionic absorption capacity when balanced, mg/g; C_e is the balanced concentration of solution, mg/L; b is the constant related to the absorbent affinity, L/mg.

Freundlich model

$$q_e = K_f (C_e)^{1/n}$$

took logarithm to both sides,

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (3)$$

In formula: q_m is the absorption capacity when balanced, mg/g, C_e is the metal concentration of balanced solution, mg/L; K_f and n are two empirical constants, for a specified absorption system, they are the function of temperature, represent absorption ability and concession absorption intensity, respectively¹⁶.

Dubinin-Radushkevich (D-R) isothermal equation

$$\ln q = \ln q_m - \beta \varepsilon^2 \quad (4)$$

ε value could be calculated by next type:

$$\varepsilon = RT \ln \left(\frac{1+q}{C_e} \right) \quad (5)$$

$$E_s = \frac{1}{\sqrt{2\beta}} \quad (6)$$

In formula: β : the constant related the absorbent energy, mol^2/kJ^2 . ε : Polanyi absorption potential, kJ/mol. C_e : balanced concentration of solution, mol/L. q , q_m : balanced absorption capacity and biggest absorption capacity, mol/g. E_s : absorption energy, kJ/mol. Fitted parameters of Langmuir and Freundlich model as shown in Table-1.

Table-1 showed that Langmuir and Freundlich model could be better fit this isothermal adsorption process, but Langmuir's fitting effect was better, saturated absorption got from Langmuir model were Pb^{2+} (378.79 mg/g) and Cu^{2+} (250 mg/g).

The order of absorbents selectively absorbed to metal ionic might have something to do with metal element negative ion, the radius of the ions and the hydration heat¹¹. Generally we think that the bigger the negative electric of metal element is, the stronger the covalent bond formed from material surface or internal oxygen atoms would be. The bigger the charge/radius ratio was, the stronger the key's formation would be. Thus, the absorption order should be $\text{Cu}^{2+} > \text{Pb}^{2+}$, but this is not corresponded with the experimental result. Because all the metal cation ions in water environment existed in the form of hydrated metal ions, so the bigger the effective hydration ion radius were, the harder the exchange reaction between the ion and internal cation ion in absorbent would be. So Pb^{2+} ions with low hydration heat's (Table-2) was easier to take off

TABLE-1
PARAMETERS OF LANGMUIR AND FREUNDLICH ISOTHERM (25 °C)

Metal ions	Langmuir model		Freundlich model			
	Correlation coefficient r	b (L/mg)	Q_m (mg/g)	K_f	1/n	Correlation coefficient r
Pb^{2+}	0.9971	0.06904	378.79	31.05	0.4981	0.9604
Cu^{2+}	0.9265	0.01516	250.0	7.23	0.6700	0.8857

TABLE-2
ELECTRO-NEGATIVITY, RADIUS, HYDRATION RADIUS
AND HYDRATION HEAT OF METAL IONS

Metal ions	Electronegativity	Radius (nm)	Effective hydration ion radius (nm)	Heat of hydration (kJ/mol)
Pb ²⁺	1.8	0.132	0.2655	1500.6
Cu ²⁺	1.9	0.073	0.2065	2119.3

complexation water and became exposed Pb²⁺ ions. This result is corresponded to Zhu *et al.*¹² research.

The above Langmuir and Freundlich model were not enough to explain the physical and chemical absorption properties of absorption process. Dubinin-Radushkevich model could be used to judge the nature of the absorption process. Fitting parameters⁹ of Dubinin-Radushkevich model were shown in Table-3.

TABLE-3
PARAMETERS OF DUBININ-RADUSHKEVICH EQUATION

Temperature (°C)	R	β (mol ² /kJ ²)	E _s (kJ/mol)
Pb ²⁺	0.9764	0.00415	10.98
Cu ²⁺	0.9107	0.0078	8.01

The E_s value in Dubinin-Radushkevich equation reflected the needed energy when exchanged 1mol ions on the surface of absorbent and when the E_s value was between 8-16 kJ/mol, it showed that, the absorption process was chemical ion-exchange; When E_s value was less than 8 kJ/mol, it showed that the absorption was physical absorption process¹³. From Table-3, the E_s value of amorphous tin(IV) phosphate absorbing Pb²⁺ and Cu²⁺ was between 8-16 kJ/mol, so the absorption mechanism was chemical ion-exchange.

Ionic strength experiment: Through ionic strength experiment, we found that, it was feasible to use the prepared material in high salinity (seawater medium) environment. In the experiment, respectively prepared 50 mL mixed solution consisted of metal ion solution with concentration of 50 mg/L, NaCl solution with concentration of 0, 0.15, 0.3, 0.6 mol/L. Then it should be conducted the absorption experiment under the same condition as discussed earlier. The result was shown in Fig. 5.

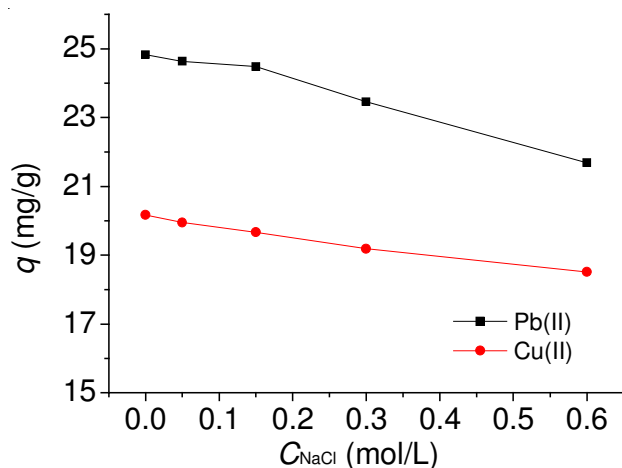


Fig. 5. Effect of NaCl concentration on the absorption of heavy metal ions with amorphous tin(IV) phosphate

Jiang *et al.*¹⁴ had researched the effect of ionic strength on natural Kaolin absorbed metal ions. When the concentration of NaNO₃ changed from 0.01-0.1 mol/L, the absorption capacity of the natural Kaolin to Pb²⁺, Cu²⁺ and Cd²⁺ was the half of before. Lin *et al.*¹⁵ used carboxymethyl chitosan to absorb Pb²⁺, with the increasing concentration of the KNO₃, the speed of the absorption was slowing down and the absorption capacity became lower and lower. Shuai *et al.*¹⁶ found that, with the increasing of the ionic strength, δ -MnO₂ and bayerite's absorption capacity of Cu²⁺ became lower. When used MX-80 clay to absorb the radioactive element Ni, the pH < 7, absorption of Ni(II) on tombarthite was obviously affected by ionic strength¹⁷ and ionic strength presented unfavorable influence.

In this study, with the increasing of the NaCl concentration, the absorption capacity had a small amount of decrease. When the concentration of NaCl solution reached 0.6 mol/L, the absorption capacity of amorphous tin(IV) phosphate to Pb²⁺ reached 21.68 mg/g, it was 87.34 % of which the absorption capacity without NaCl. And the absorption capacity to Cu²⁺ still reached 18.51 mg/g, it was 91.77 % of which the absorption capacity without NaCl, it explained that, to system ionic strength, it existed adverse effects on amorphous tin(IV) phosphate's absorption with Pb²⁺ and Cu²⁺, but the range of the impact was not too much.

The salinity of known seawater is *ca.* 3 % (equal to the concentration of NaCl was 0.5 mol/L) and in this study the set concentration of NaCl was between 0-0.6 mol/L. So, it was feasible to use amorphous tin(IV) phosphate to remove the Pb²⁺ and Cu²⁺ from marine culture wastewater.

Study of thermodynamics: Gibbs free energy (ΔG°) is a standard that measure the reaction spontaneous carrying on. If the ΔG° is negative, it explains that it is spontaneous carrying on at a certain temperature. In the absorption reaction, free energy alternation ΔG° is related to the equilibrium constant k and existing the following relation:

$$\Delta G^\circ = -RT \ln k \quad (7)$$

In the formula: ΔG° is the free energy alternation, kJ/mol; R is the gas reaction constant, 8.314 J/(mol K); T is the absolute temperature, K; $k = b \times M \times 1000$, b is Langmuir constant, M is the atomic weight of the metal.

After calculation, the ΔG° of amorphous tin(IV) phosphate absorbing Pb²⁺ and Cu²⁺ were -23.71 and -17.02 kJ/mol, respectively. It proved that, amorphous tin(IV) phosphate's absorption to Pb²⁺ and Cu²⁺ was a spontaneous process and the spontaneity of Pb²⁺'s absorption was stronger.

Potentiometric titration experiment: Blank experiment: added 50 mL 0.1 mol/L NaCl solution to the beaker, then added 0.01 mol/L NaOH solution to adjust the pH, used the potentiometric titrimeter to titrate the pH at 9, then stopped titrating. In the first, respectively added 0.1 g amorphous tin(IV) phosphate and 25 mL 100 mg/L metal ion standard solution to the NaCl solution and then added the before two substances at the same time, then used the potentiometric titrimeter to titrate.

Took the volume of the adding NaOH solution as abscissa, used the pH as ordinate to draw diagrams, obtained the blank titration curve Fig. 6 and the titration curve Figs. 7 and 8 when existing Pb²⁺ and Cu²⁺, respectively.

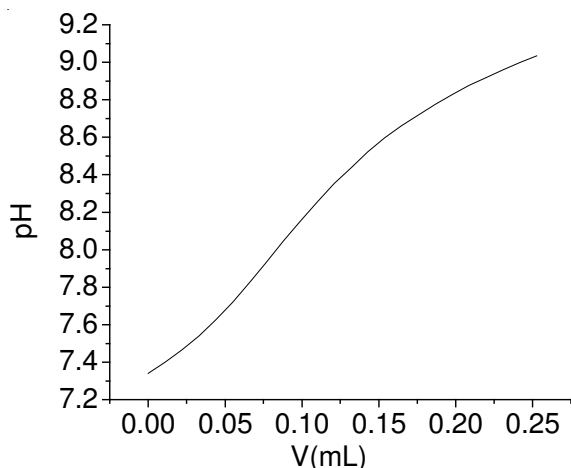
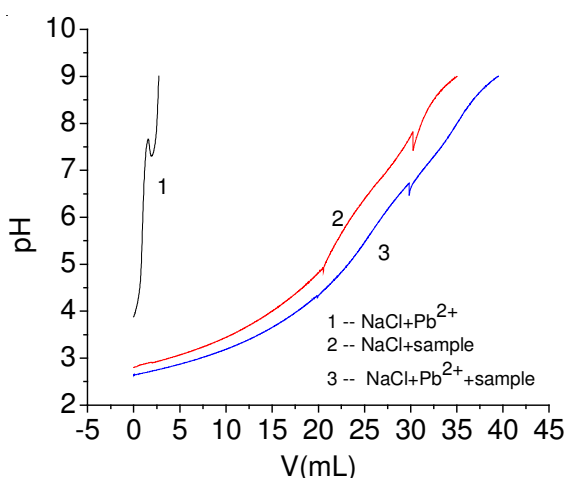
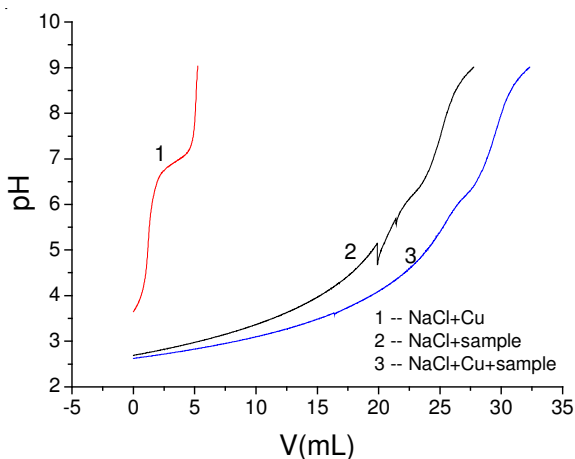


Fig. 6. pH-titration at the media of NaCl (blank titration)

Fig. 7. pH titration curve at the media of NaCl and Pb^{2+} Fig. 8. pH titration curve at the media of NaCl and Cu^{2+}

Compared with the curve of blank experiment, it could be found out that the pH of the system is dramatic decline after adding amorphous tin(IV) phosphate. And when adding amorphous tin(IV) phosphate and metal ions at the same time, the pH of the system declined more. It proved that the absorption mechanism of the process was the ion-exchange reaction between heavy metal ions and H^+ in the sample.

Conclusion

The best pH of amorphous tin(IV) phosphate absorbing Pb^{2+} and Cu^{2+} is 5. The balance time is, respectively at 6 and 8 h. At 25 °C, the process of amorphous tin(IV) phosphate absorbing Pb^{2+} and Cu^{2+} match the Langmuir isothermal formula well. The saturated extent of absorption is, respectively 378.79 and 250 mg/g. The process of amorphous tin(IV) phosphate absorbing Pb^{2+} and Cu^{2+} is a chemical ionic exchange process. The absorption mechanism is that H^+ of amorphous tin(IV) phosphate conduct an exchange reaction with metal ions in solution. Ion strength experiment shows that, it is completely feasible to remove lead(II) and copper(II) from hypersaline media with amorphous tin(IV) phosphate (such as marine culture wastewater).

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