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Equilibrium of hydroxyl complex ions in Pb^{2+}-H_2O system

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Abstract: The thermodynamics equilibrium principle was used to construct the diagrams for the concentration of complex ions (p*c*) vs pH, the distribution ratio of lead hydroxyl complex ions (α_n) vs pH, and the conditional solubility product of $Pb(OH)_2$ vs pH in the Pb^{2+}-H_2O system. The relationship between the equilibrium concentration of each kind of lead hydroxyl complex ions in equilibrium with $Pb(OH)_2$(s) and pH value was shown in the system. The minimum solubility of lead is at the pH value of 10.096−10.997. The distribution ratio of each kind of the lead hydroxyl complex ions is determined as a function of the pH value and the total lead concentration ($[Pb]_T$). The diagram for the conditional solubility product, pK_{SP} vs pH, shows that each kind of lead hydroxyl complex ions existing in the system is dependent upon an optimized pH value at the established concentration of $[Pb]_T$, and that pK_{SP} reaches the minimum at the pH value of 10.3−11.2. The results can provide a theoretical basis for removing lead ions from wastewater by the neutralization and hydrolyzation technology.

Key words: Pb^{2+}-H_2O system; lead-containing wastewater; diagram of p*c*—pH; thermodynamics equilibrium principle

1 Introduction

Heavy metals are known to be detrimental to the living beings. The toxic heavy metal ions in industrial wastewaters have been considerably concerned in recent years[1]. These important contaminants are discharged from many industry fields such as electroplating, dyes and dye intermediates, textiles, tanneries, oil refineries, mining and smelters. It has been observed that increased concentration of heavy metals in the aquatics environments can cause phyto toxicity, bio-concentration and bio-magnification by organisms. Lead is hazardous and highly toxic to humans, plants and animals. Primary health effects due to Pb(Ⅱ) poisoning are nervous and renal breakdown, weakness, headache, brain damage, convulsions, behavioral disorders and constipation. Lead is a substitute for calcium in bony tissues and accumulates there. The presence of lead in drinking water is known to cause various types of serious health problems, leading to death in extreme cases[2−4].

Removal of heavy metal-bearing industrial effluents has become one of the primary challenges of wastewater treatment. Filtration, adsorption, reverse osmosis, solvent extraction, and membrane separation techniques are used for removal and recovery of heavy metals from industrial wastewater. The neutralization and metal hydroxide precipitation are the conventional techniques[5−6]. In order to offer theoretical foundation for neutralization, thermodynamic analysis of lead ion hydrolyzation has been carried out, but either all kinds of lead hydroxyl complex ions are ignored[7−8] or only single kind of complex ion is considered[9−12]. As a result, the incomplete conclusion would lead to the incorrect guidance for the technology[13−14]. It is necessary to construct the complete equilibrium diagrams of Pb^{2+}-H_2O system based on the equilibrium of various kinds of complex ions.

In this study, thermodynamic equilibria of hydroxyl complex ions in Pb^{2+}-H_2O system were analyzed and diagrams for the concentration of complex ions (p*c*) vs pH, the distribution ratio of the lead hydroxyl complex ions (α_n) vs pH, and the conditional solubility product of $Pb(OH)_2$ (pK_{SP}) vs pH in Pb^{2+}-H_2O system, were res-

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pectively drawn based on the simultaneous equilibria of all complex ions[15−19]. The aim is at exploring the various forms of the lead species existing in aqueous solution and the rule of change in solubility of $Pb(OH)_2$ with the pH value, and determining the minimum solubility of $Pb(OH)_2$ and the optimum range of pH value. These diagrams have more advantages over pE—pH diagram in the neutralization and metal hydroxide precipitation process[20−21].

2 Effect of pH value on coordination equilibrium of lead hydroxyl complex ions

Assuming that there are only six kinds of lead hydroxyl complex ions, that is, $PbOH^+$, $Pb(OH)_2$, $Pb(OH)_3^-$, Pb_2OH^{3+}, $Pb_4(OH)_4^{4+}$ and $Pb_6(OH)_8^{4+}$ in lead-containing wastewater, correspondingly the cumulative formation constants for them at 298.15 K are as follows [22−23]:

$$Pb^{2+}+OH^-=PbOH^+$$

$$K_1=\frac{[PbOH^+]}{[Pb^{2+}][OH^-]}=10^{6.2} \quad (1)$$

$$Pb^{2+}+2OH^-=Pb(OH)_2$$

$$K_2=\frac{[Pb(OH)_2]}{[Pb^{2+}][OH^-]^2}=10^{10.3} \quad (2)$$

$$Pb^{2+}+3OH^-=Pb(OH)_3^-$$

$$K_3=\frac{[Pb(OH)_3^-]}{[Pb^{2+}][OH^-]^3}=10^{13.3} \quad (3)$$

$$2Pb^{2+}+OH^-=Pb_2(OH)^{3+}$$

$$K_4=\frac{[Pb_2(OH)^{3+}]}{[Pb^{2+}]^2[OH^-]}=10^{7.6} \quad (4)$$

$$4Pb^{2+}+4OH^-=Pb_4(OH)_4^{4+}$$

$$K_5=\frac{[Pb_4(OH)_4^{4+}]}{[Pb^{2+}]^4[OH^-]^4}=10^{36.1} \quad (5)$$

$$6Pb^{2+}+8OH^-=Pb_6(OH)_8^{4+}$$

$$K_6=\frac{[Pb_6(OH)_8^{4+}]}{[Pb^{2+}]^6[OH^-]^8}=10^{69.3} \quad (6)$$

It is known that

$$Pb(OH)_2(s)=Pb^{2+}+2OH^-$$

$$K_{S0}=[Pb^{2+}][OH^-]^2=1.2\times10^{-15} \quad (7)$$

Multiplying Eqs.(1)−(6) by Eq.(7), respectively, the following equations can be obtained:

$$Pb(OH)_2(s)=PbOH^++OH^-$$

$$K_{S1}=[PbOH^+][OH^-]=1.902\times10^{-9} \quad (8)$$

$$Pb(OH)_2(s)=Pb(OH)_2$$

$$K_{S2}=[Pb(OH)_2]=2.394\times10^{-5} \quad (9)$$

$$Pb(OH)_2(s)+OH^-=Pb(OH)_3^-$$

$$K_{S3}=\frac{[Pb(OH)_3^-]}{[OH^-]}=2.394\times10^{-2} \quad (10)$$

$$2Pb(OH)_2(s)=Pb_2(OH)^{3+}+3OH^-$$

$$K_{S4}=[Pb_2(OH)^{3+}][OH^-]^3=5.733\times10^{-23} \quad (11)$$

$$4Pb(OH)_2(s)=Pb_4(OH)_4^{4+}+4OH^-$$

$$K_{S5}=[Pb_4(OH)_4^{4+}][OH^-]^4=2.610\times10^{-24} \quad (12)$$

$$6Pb(OH)_2(s)=Pb_6(OH)_8^{4+}+4OH^-$$

$$K_{S6}=[Pb_6(OH)_8^{4+}][OH^-]^4=5.958\times10^{-21} \quad (13)$$

Taking the logarithm of both sides of Eqs.(7)−(13) gives

$$\lg K_{S0}=\lg[Pb^{2+}]+2\lg[OH^-]=\lg[Pb^{2+}]+2\lg K_w+2pH$$
$$p[Pb^{2+}]=-13.073+2pH \quad (14)$$

$$\lg K_{S1}=\lg[PbOH^+]+\lg[OH^-]=\lg[PbOH^+]+\lg K_w+pH$$
$$p[PbOH^+]=-5.276+pH \quad (15)$$

$$\lg K_{S2}=\lg[Pb(OH)_2]$$
$$p[Pb(OH)_2]=4.621 \quad (16)$$

$$\lg K_{S3}=\lg[Pb(OH)_3^-]-\lg[OH^-]=\lg[Pb(OH)_3^-]-\lg K_w-pH$$
$$p[Pb(OH)_3^-]=15.618-pH \quad (17)$$

$$\lg K_{S4}=\lg[Pb_2(OH)^{3+}]+3\lg[OH^-]=\lg[Pb_2(OH)^{3+}]+3\lg K_w+3pH$$
$$p[Pb_2(OH)^{3+}]=-19.749+3pH \quad (18)$$

$$\lg K_{S5}=\lg[Pb_4(OH)_4^{4+}]+4\lg[OH^-]=\lg[Pb_4(OH)_4^{4+}]+4\lg K_w+4pH$$
$$p[Pb_4(OH)_4^{4+}]=-32.405+4pH \quad (19)$$

$$\lg K_{S6}=\lg[Pb_6(OH)_8^{4+}]+4\lg[OH^-]=\lg[Pb_6(OH)_8^{4+}]+4\lg K_w+4pH$$
$$p[Pb_6(OH)_8^{4+}]=-35.763+4pH \quad (20)$$

The concentration of OH^- is calculated at a given pH based on the water ionization equation and the concentration of Pb^{2+} is determined by Eq.(14). The latter is used in Eq.(15) to calculate $[PbOH^+]$, and in turn continue until the concentration of each complex is known. These values as functions of the pH value are plotted in Fig.1, which constructs the pc—pH diagram of Pb^{2+}-H_2O system.

The lines in Fig.1 represent the relationship between the equilibrium concentration of the complex ions and the pH value. The right-upper area surrounded by these lines (e.g. the cross-hatching area) is the stable zone of $Pb(OH)_2$(s). Boundaries constituting this stable zone can illustrate approximately the relationship between the total solubility of Pb^{2+} and the pH value. Fig.1 illustrates that Pb^{2+} is the predominant soluble species at the low pH, and $Pb_6(OH)_8^{4+}$ is the predominant species at the high pH. Obviously, if complex formation were ignored and lead solubility were calculated solely by use of Eq.(7), an erroneous conclusion could be drawn. From

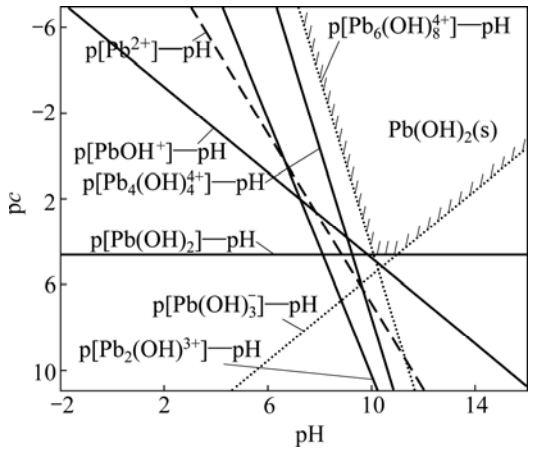

Fig.1 Diagram of p*c*—pH of Pb^{2+}-H_2O system at 298.15 K

Fig.1, it can be seen that the minimum solubility of lead is 4.959 mg/L at the pH value of 10.096−10.997, beyond which the solubility of lead will increase.

3 Effect of pH value on species of lead hydroxyl complex ions

Complex formation also affects the solubility of salts. Lead is commonly removed from acidic wastewaters by adding lime-milk to form the insoluble $Pb(OH)_2$(s). However, if excess base is added, lead will form soluble complexes with OH^- and will return to or remain in solution. In aqueous solution, lead hydroxyl complex ions of $PbOH^+$, $Pb(OH)_2$, $Pb(OH)_3^-$, $Pb_2(OH)^{3+}$, $Pb_4(OH)_4^{4+}$ and $Pb_6(OH)_8^{4+}$ may exist. From Eqs.(1)−(6), the following equations can be deduced:

$$\frac{[PbOH^+]}{[Pb^{2+}]}=K_1\cdot[OH^-] \tag{21}$$

$$\frac{[Pb(OH)_2]}{[Pb^{2+}]}=K_2\cdot[OH^-]^2 \tag{22}$$

$$\frac{[Pb(OH)_3^-]}{[Pb^{2+}]}=K_3\cdot[OH^-]^3 \tag{23}$$

$$\frac{[Pb_2(OH)^{3+}]}{[Pb^{2+}]^2}=K_4\cdot[OH^-] \tag{24}$$

$$\frac{[Pb_4(OH)_4^{4+}]}{[Pb^{2+}]^4}=K_5\cdot[OH^-]^4 \tag{25}$$

$$\frac{[Pb_6(OH)_8^{4+}]}{[Pb^{2+}]^6}=K_6\cdot[OH^-]^8 \tag{26}$$

In addition, a mass balance for lead in solution is

$$[Pb]_T=[Pb^{2+}]+[PbOH^+]+[Pb(OH)_2]+[Pb(OH)_3^-]+2[Pb_2(OH)^{3+}]+4[Pb_4(OH)_4^{4+}]+6[Pb_6(OH)_8^{4+}] \tag{27}$$

$[Pb]_T$ represents the total soluble concentration of lead, i.e. the solubility of lead.

Definition of parameters, α_{0-6}, is as follows:

$$\alpha_0=\frac{[Pb^{2+}]}{[Pb]_T} \tag{28}$$

$$\alpha_1=\frac{[PbOH^+]}{[Pb]_T} \tag{29}$$

$$\alpha_2=\frac{[Pb(OH)_2]}{[Pb]_T} \tag{30}$$

$$\alpha_3=\frac{[Pb(OH)_3^-]}{[Pb]_T} \tag{31}$$

$$\alpha_4=\frac{2[Pb_2(OH)^{3+}]}{[Pb]_T} \tag{32}$$

$$\alpha_5=\frac{4[Pb_4(OH)_4^{4+}]}{[Pb]_T} \tag{33}$$

$$\alpha_6=\frac{6[Pb_6(OH)_8^{4+}]}{[Pb]_T} \tag{34}$$

Substitution of Eqs.(21)−(26) and Eq.(28) into Eqs.(29)−(34) gives

$$\alpha_1=\frac{[Pb(OH)^+]}{[Pb]_T}=\frac{[Pb^{2+}]}{[Pb]_T}\cdot\frac{[PbOH^+]}{[Pb^{2+}]}=\alpha_0\cdot K_1\cdot[OH^-] \tag{35}$$

$$\alpha_2=\frac{[Pb(OH)_2]}{[Pb]_T}=\frac{[Pb^{2+}]}{[Pb]_T}\cdot\frac{[Pb(OH)_2]}{[Pb^{2+}]}=\alpha_0\cdot K_2\cdot[OH^-]^2 \tag{36}$$

$$\alpha_3=\frac{[Pb(OH)_3^-]}{[Pb]_T}=\frac{[Pb^{2+}]}{[Pb]_T}\cdot\frac{[Pb(OH)_3^-]}{[Pb^{2+}]}=\alpha_0\cdot K_3\cdot[OH^-]^3 \tag{37}$$

$$\alpha_4=\frac{2[Pb_2(OH)^{3+}]}{[Pb]_T}=\frac{[Pb^{2+}]^2}{[Pb]_T}\cdot\frac{2[Pb_2(OH)^{3+}]}{[Pb^{2+}]^2}=2\alpha_0^2\cdot K_4\cdot[OH^-]\cdot[Pb]_T \tag{38}$$

$$\alpha_5=\frac{4[Pb_4(OH)_4^{4+}]}{[Pb]_T}=\frac{[Pb^{2+}]^4}{[Pb]_T}\cdot\frac{4[Pb_4(OH)_4^{4+}]}{[Pb^{2+}]^4}=4\alpha_0^4\cdot K_5\cdot[OH^-]^4\cdot[Pb]_T^3 \tag{39}$$

$$\alpha_6=\frac{6[Pb_6(OH)_8^{4+}]}{[Pb]_T}=\frac{[Pb^{2+}]^6}{[Pb]_T}\cdot\frac{6[Pb_6(OH)_8^{4+}]}{[Pb^{2+}]^6}=6\alpha_0^6\cdot K_6\cdot[OH^-]^8\cdot[Pb]_T^5 \tag{40}$$

Inserting Eq.(28) and Eqs.(35)−(40) into Eq.(27) gives

$$\alpha_0=(1+K_1\cdot[OH^-]+K_2\cdot[OH^-]^2+K_3\cdot[OH^-]^3+2\alpha_0K_4[OH^-]\cdot[Pb]_T+4\alpha_0^3K_5[OH^-]^4\cdot[Pb]_T^3+6\alpha_0^5K_6[OH^-]^8\cdot[Pb]_T^5)^{-1} \quad (41)$$

From the above equations, it can be concluded that the concentration ratio of each ions depends greatly on the pH value and total lead concentration. Supposing that $[Pb]_T$ is 10^{-4} mol/L and 10^{-2} mol/L, respectively, substituting the different pH values into Eq.(41) gives the corresponding α_0; similarly, α_1, α_2, α_3, α_4, α_5 and α_6 can be calculated according to Eqs.(35)−(40). Fig.2 shows the diagram of the ratio of lead hydroxyl complex ions as functions of the pH value.

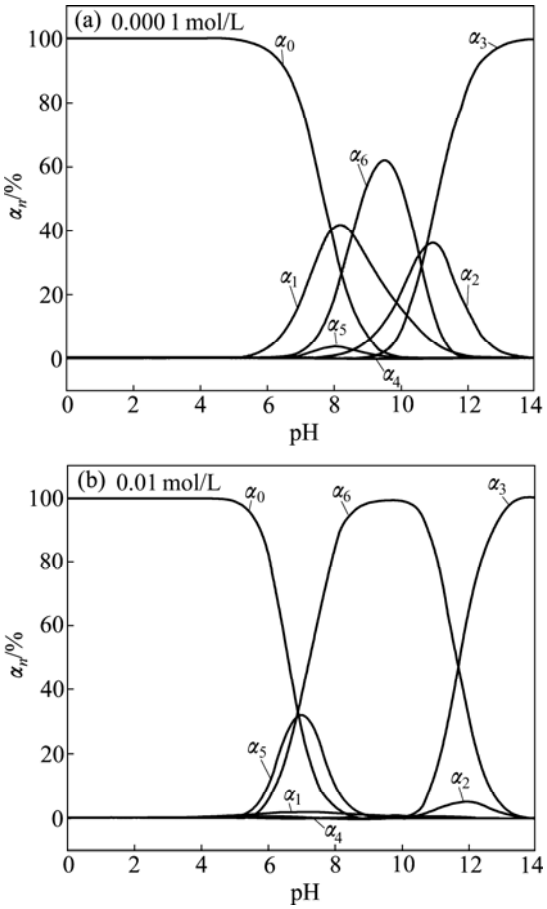

Fig.2 α_n—pH diagrams illustrating ratio of lead hydroxyl complex ions as function of pH value

The various kinds of species of the different lead hydroxyl complex ions exist in the solution with the different pH values. Lead ion exists mainly in free state and a slight amount of $PbOH^+$ ($[Pb]_T$=0.000 1 mol/L) or $Pb_4(OH)_4^{4+}$ ($[Pb]_T$ =0.01 mol/L) at the pH value below 7.0. Their concentrations increase gradually with pH value declining. When the pH value is in the range of 8.0−11.0, $Pb_6(OH)_8^{4+}$ is dominant, together with a small quantity of $PbOH^+$ ($[Pb]_T$=0.000 1 mol/L) or $Pb(OH)_2$ ($[Pb]_T$=0.000 1 mol/L). The more the total concentration of lead, the more the concentration of $Pb_6(OH)_8^{4+}$. $Pb(OH)_3^-$ is the primary species with a small quantity of $Pb(OH)_2$ and $Pb_6(OH)_8^{4+}$ at the pH value over 12.0. There is an evident effect of total concentration of lead on the concentration of the different lead hydroxyl complex ions.

4 Effect of pH value on solubility of $Pb(OH)_2$

Lead can form polynuclear complexes containing two or more lead atoms, which will make the solubility of $Pb(OH)_2$ increase. Effect of the pH value on solubility of $Pb(OH)_2$ can be expressed by the conditional solubility product[9].

The conditional solubility product of $Pb(OH)_2$(s) is defined as

$$K_{SP}=[Pb]_T\cdot[OH^-]_T^2 \quad (42)$$

where $[Pb]_T$ represents the total lead concentration, i.e. the solubility of lead (Eq.(27)). $[Pb^{2+}]$, $[PbOH^+]$, $[Pb(OH)_2]$, $[Pb(OH)_3^-]$, $[Pb_2(OH)^{3+}]$, $[Pb_4(OH)_4^{4+}]$ and $[Pb_6(OH)_8^{4+}]$ can be calculated from Eqs.(7)−(13). Inserting these values into Eq.(27) can determine the total concentration of soluble lead.

The mass balance of OH^- is:

$$[OH^-]_T=[OH^-]+[Pb(OH)^+]+2[Pb(OH)_2]+3[Pb(OH)_3^-]+[Pb_2(OH)^{3+}]+4[Pb_4(OH)_4^{4+}]+8[Pb_6(OH)_8^{4+}] \quad (43)$$

where $[OH^-]_T$ represents the total concentration of OH^-.

The conditional solubility product of $Pb(OH)_2$(s) at the different pH can be calculated by combination of Eq.(27), Eq.(42) and Eq.(43), and the results are shown in Fig.3. Simultaneously, the conditional solubility product of $Pb(OH)_2$ is also drawn.

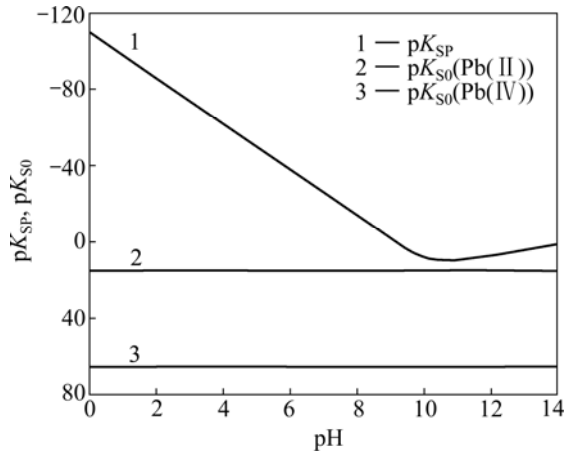

Fig.3 Relationship between conditional solubility product of $Pb(OH)_2$ and pH value

The area above the curve is the supersaturation region of $Pb(OH)_2$(s) dissolution, where $Pb(OH)_2$ precipitation occurs, while other regions are unsaturated ones. Fig.3 indicates that the minimum solubility of

$Pb(OH)_2$ is in the pH range of 10.3−11.2, beyond which the solubility product of $Pb(OH)_2$ increases obviously. In addition, pK_{S0} locates at the unsaturated region, which indicates that lead in wastewater cannot be removed to the minimum concentration determined by the solubility product of $Pb(OH)_2$ using the neutralization and hydrolyzation method.

5 Conclusions

1) In Pb^{2+}-H_2O system, the diagrams for the concentration of the lead complex ions, the distribution ratio of lead hydroxyl complex ions and the conditional solubility product of $Pb(OH)_2$ as a function of the pH value are respectively constructed based on the thermodynamics equilibrium principle.

2) The pc vs pH diagram represents the relationship between the equilibrium concentration of the complex ions in equilibrium with $Pb(OH)_2$(s) and the pH value. The minimal solubility of lead is 4.959 mg/L at the pH value of 10.096−10.997, beyond which the solubility of lead will increase.

3) The α_n—pH diagram shows the distribution ratio of the lead hydroxyl complex ions as a function of the pH value. For each kind of the lead hydroxyl complex ions, there is an optimum pH value scope.

4) The pK_{SP}—pH diagram shows the relationship between the conditional solubility product of $Pb(OH)_2$ and the pH value. The minimum solubility of $Pb(OH)_2$ is in the pH range of 10.3−11.2, beyond which the conditional solubility product of $Pb(OH)_2$ increases obviously.

References

[1] DOYURUM S, CELIK A. Pb(Ⅱ) and Cd(Ⅱ) removal from aqueous solutions by olive cake [J]. Journal of Hazardous Materials, 2006, 138(1/2): 22−28.

[2] GABALLAH I, KILBERTUS G. Recovery of heavy metal ions through decontamination of synthetic solutions and industrial effluents using modified barks [J]. Journal of Geochemical Exploration, 1998, 62(1/3): 241−286.

[3] LOW K S, LEE C K, LIEW S C. Sorption of cadmium and lead from aqueous solutions by spent grain [J]. Process Biochemistry, 2000, 36(1/2): 59−64.

[4] BULUT Y, BAYSAL Z. Removal of Pb(Ⅱ) from wastewater using wheat bran [J]. Journal of Environmental Management, 2006, 78(2): 107−113.

[5] XIE Hong-bin. Study on neutralized method to treating heavy metal wastewater [J]. Hunan Nonferrous Metals, 2000, 16(9): 91−92.

[6] DENG Li-ping, SU Ying-ying, SU Hua, WANG Xin-ting, ZHU Xiao-bin. Sorption and desorption of lead(Ⅱ) from wastewater by green algae *Cladophora fascicularis* [J]. Journal of Hazardous Materials, 2007,143(1/2): 220−225.

[7] ZHONG Zhu-qian, MEI Guang-gui, HE Qing-pu. Theoretical analysis of purification of wastewater by neutralization and hydrolyzation [J]. Nonferrous Smelt, 1981(4): 44−51. (in Chinese)

[8] YAO Qing-song. The effect of equilibrium theory on treating heavy metals wastewater by chemical methods [J]. Pollution and Preventing Technology, 1994(12): 10−12. (in Chinese)

[9] LI Bo. Thermodynamics analysis on the precipitation process of metal carbonates [J]. Rare Metals and Cemented Carbides, 2005, 32 (6): 4−8. (in Chinese)

[10] GAI Qing-chun, GUO Yan-he, LI Su-qi, LIN Hua-kuan, WANG Xu, ZHU Shou-rong, CHEN Rong-ti. Thermodynamic properties of complexes of 1,3,5-tri (n-2,5-diaminonhexaane)-bebzene with Co(Ⅱ), Ni(Ⅱ), Cu(Ⅱ), Zn(Ⅱ) [J]. Acta Scientiarum Naturalium Universitatis Nankaiensis, 2001, 34(2): 13−19. (in Chinese)

[11] GAO Dong-zhao, GUO Yan-he, ZHU Shou-rong, LIN Hua-kuan, XU Xin-he. Thermodynamic studies on a new type of carboxamide metal complexs [J]. Chemical Journal of Chinese University, 2004, 25(4): 740−742. (in Chinese)

[12] DRIESNER T, HA T K, SEWARD T M. Oxygen and hydrogen isotope fractionation by hydration complexes of Li^+, Na^+, K^+, Mg^{2+}, F^-, Cl^-, and Br^-: A theoretical study [J]. Geochimica et Cosmochimica Acta, 2000, 64(17): 3007−3033.

[13] ARMADA M P G. A program for calculation and graphic representation of conditional constants(Ⅱ): Solubility products [J]. Computers Chem, 1996, 20(3): 385−387.

[14] HOU Miao-lin, BAUGHMAN G L. Predicting the precipitation of acid and direct dyes in natural waters [J]. Dyes and Pigments, 1992, 18(1): 35−46.

[15] ZHANG Xiang-lin, KANG Heng. Coordination chemistry [M]. Changsha: Central South University of Technology Press, 1986.

[16] STUMM W, MORGAN J J. Aquatic chemistry—An introduction to emphasizing chemical equilibria in natural waters [M]. TANG Hong-xiao. Beijing: Science Press, 1987.

[17] WANG Qing-cheng, HE Wen-meng, YIN Guang-fu. Evaluation ionic distribution for the complicated complex equilibrium by means of trial-iteration [J]. Journal of Sichuan University: Natural Science Edition, 2000, 37(6): 906−910. (in Chinese)

[18] ZHANG Ping-min. Advanced chemistry for engineering [M]. Changsha: Hunan Education Press, 2002.

[19] LI Ke-an, WEI Yong-ju, LIU Feng, SUN Bi-yun, TONG Shen-yang. Spectophotometric study on the complexation equilibria of Pb(Ⅱ) and Zn(Ⅱ) with 5-Br-PADAP [J]. Universitatis Pekinensis: Acta Scientiarum Naturalium, 1994, 30(6): 655−658. (in Chinese)

[20] TROJANOWICZ M, ALEXANDER P W, HIBBERT D B. Flow-injection potentiometric determination of free cadmium ions with a cadmium ion-selective electrode [J]. Analytica Chimica Acta, 1998, 370(2): 267−278.

[21] CHEN Ding-wang, RAY A K. Removal of toxic metal ions from wastewater by semiconductor photocatalysis [J]. Chemical Engineering Science, 2002, 56(11): 1561−1570.

[22] FANG Jing-li. Electroplating of multi-coordination [M]. Beijing: National Defence Industry Press, 1985.

[23] CHEN Shao-yan. Aquatic chemistry [M]. Beijing: Irrigation and Electrics Press, 1989.

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