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Chelation of heavy metals by potassium butyl dithiophosphate

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Abstract

Potassium butyl dithiophosphate (PBD) was developed and introduced as a new chelating agent for heavy metal removal. The synthesized PBD were characterized by IR and NMR. The effects of pH, chelating agent dosage, and other heavy metal ions on the performance of PBD in Cd^{2+} removal from water are investigated. Experimental results showed that the chelating agent could be used to treat acidic heavy metal wastewater. The Cd^{2+} removal was not affected by solution pH value within the range of 2 to 6. The Cd^{2+} removal rate could reach over 99%. Therefore, the deficiency of the precipitation process using hydroxide under alkaline condition can be overcome. Without the need for pH adjustment, the method could save on costs. If Cd^{2+} co-exists with Pb^{2+} and Cu^{2+}, the affinity of the chelating agent with these three heavy metal ions was in the order of: $Cu^{2+} > Pb^{2+} > Cd^{2+}$. Through PBD chelating precipitation, all the contents of Pb^{2+}, Cd^{2+}, and Cu^{2+} in wastewater met the standard levels through a one-step treatment. The one-step treatment process was superior to the process (sectional treatment is required) of precipitation with hydroxide. When the pH was between 3 and 11, the amount of leached chelated Cd^{2+} was much lower than that obtained by precipitation with hydroxide. Therefore, the risk of environmental pollution could be further reduced.

Key words: chelation; heavy metal; precipitation; stability; wastewater

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Introduction

Heavy metal waste is a common subject in environmental research because of the complexity of its chemical behavior and its ecological effects. The importance of research on protection against heavy metal pollution is widely acknowledged because of the various resulting diseases and effects, including the "Minamata disease" caused by mercury pollution and the "Itai-itai disease" caused by cadmium pollution. Various methods have been developed to treat wastewaters containing heavy metals, including precipitation with hydroxide and sulfuration, ion-exchange, electrolysis, adsorption, reverse osmosis, and biological treatment (Meng and Hu, 1991; Ma and Zhang, 2007). For the sake of technical and economic reasons, precipitation with hydroxide is the most frequently used method for heavy metal wastewater remediation (Wang and Chang, 2007). However, this course of treatment is not ideal because different heavy metal hydroxides precipitate at different pH levels. During treatment process, some ions may bond with other ions in solution, when pH decreases, heavy metal ions escape from the precipitates and cause secondary pollution. Because the composition of heavy metal wastewaters becomes increasingly complicated, requirements for wastewater discharge become stricter, and the conventional method of precipitation becomes inadequate (Xu and Zhang, 2006).

Studies on organic chelating agents have been conducted for heavy metal removal from wastewater (Navarro et al., 1998; Matlock et al., 2001a; Andreottola et al., 2007). A chelating agent can bond with heavy metal ions to form stable and insoluble chelated products, removing effectively heavy metals from the solution. At present, dithiocarbamate and its derivatives are the most thoroughly studied heavy metal chelating agents. They have been applied in the removal of heavy metal from wastewaters and treatment of fly ash (Jiang et al., 2004; Li et al., 2004). Pyridine-thiol and 1,3-benzenediamidoethanethiol are two new chelating agents. 1,3-Benzenediamidoethanethiol has been applied in the treatment of acid mine wastewater (Matlock et al., 2001b, 2002). Removal of heavy metal from water through an organic chelating agent has been a focus of international environmental research. This article presented the synthesis of the new chelating agent patassium bytyl dithiophosphate (PBD) and the mechanism through which it chelates heavy metals. Factors influencing the treatment of cadmium-containing wastewater

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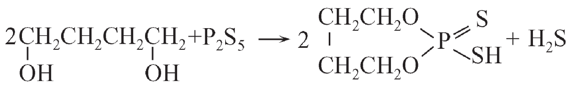
with PBD were investigated. The stability of the chelated products was analyzed, and a theoretical and practical foundation was developed for industrial applications.

1 Materials and methods

1.1 Synthesis of chelating agent

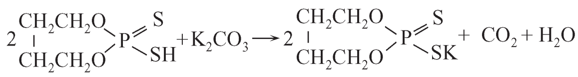
Phosphorus pentasulfide and 1,4-butanediol were first reacted to synthesize butyl dithiophosphoric ester according to the following Reaction (1):



(1)

In a reaction kettle containing 222 g (1 mol) of solid phosphorus pentasulfide, 1,4-butanediol was slowly added at a mole ratio of 1:2.5–3 (phosphorus pentasulfide:1,4-butanediol). After the 1, 4-bulanediol addition, the reaction temperature was increased from 25–35 to about 80°C. Evolved H_2S was absorbed in an alkaline solution. After continuous stirring for 5–8 hr, the reaction liquid was fractionally distilled under reduced pressure (5 mmHg). Pure butyl dithiophosphoric ester was collected within a narrow boiling-temperature range (90.5–91.0°C).

Potassium alkali metal was added as a substitute for the proton of the butyl dithiophosphoric ester, resulting in the corresponding salt (heavy metal chelating agent). The reaction, with the addition potassium carbonate as an example is as follows (Raction (2)):



(2)

Potassium hydroxide or potassium carbonate was slowly added into a reaction kettle containing the butyl dithiophosphoric ester liquid. The mole ratio of potassium hydroxide added to the phosphorus pentasulfide for the synthesis of butyl dithiophosphoric ester was 2–3:1, while the mole ratio of potassium carbonate added to phosphorus pentasulfide was 1–1.5:1. After the solution was stirred for 3–5 hr, ethanol was added to dissolve the product. The volume ratio of ethanol to the product in the kettle was 3:1. After filtration and when the ethanol has been distilled out at a normal pressure, the PBD product was obtained. To improve the purity of the product, product dissolution in ethanol followed by evaporation can be repeated 2 to 3 times.

1.2 Effects of treatment condition

A wastewater sample containing Cd^{2+} was prepared. A total of 500 mL wastewater was sampled under controlled reaction conditions (pH, amount of PBD added, co-existence of Cd^{2+}, Cu^{2+}, and Pb^{2+}, and stirring rate). The sample was stirred for 10 min after addition of PBD, and the flocculating constituents were precipitated. The solution was cleared through a membrane filter with a pore diameter of 0.42 μm. The concentration of heavy metal ions in the filtrate was measured using an atomic absorption spectrophotometer. The influences of pH value, amount of chelating agent added, and heavy metal ion co-existence on heavy metal removal were evaluated. The influence of the stirring rate on the precipitation performance of the chelated product was also analyzed. PBD was prepared in 5 wt.% solutions before adding to the wastewater. Because only a small volume of PBD solution was added into the wastewater, the volume of wastewater after PBD addition did not change. The experimental conditions are shown in Table 1.

1.3 Stability of chelated products

The Cd^{2+} precipitates from the chelating agent and sodium hydroxide were dried at 40°C, and 10 g of precipitate was added separately into 100 mL of the solution at pH values of 3, 5, 7, 9, and 11. The mixture was filtered after stirring for 6 hr. The Cd^{2+} concentration in each filtrate type was measured to determine the amount of precipitates that leached from the chelated products.

1.4 Experimental materials

Wastewater containing heavy metals was prepared with $CdCl_2$, $CuCl_2$, and $Pb(NO_3)_2$. The standard sample adopted in heavy metal concentration measurement was obtained from China National Environmental Monitoring Centre. The solution pH was adjusted with HNO_3 or NaOH. All reagents used were of analytical grade.

1.5 Experimental instruments

Atomic absorption spectrophotometer TAS-986 (Beijing Purkinje General Instrument Co., Ltd., China), Fourier transform infrared (FT-IR) spectrometer IRPrestige-21 (Shimadzu Corporation, Japan), elemental analyzer Vario EL (Elementar, Germany), and nuclear magnetic resonance (NMR) spectroscope Avance 400 (Bruker Corporation, Switzerland) was used in the experiment.

Table 1 Experimental conditions

Experiments	Initial concentration of wastewater (mg/L)	pH	Stirring rate (r/min)	PBD concentration (mg/L)
Influence of pH	Cd^{2+}: 100	2–6	100	495
Influence of amount of PBD added	Cd^{2+}: 25; 50; 100	5.0	100	34–720
Selectivity of PBD to metal ions	Cd^{2+}: 56; Pb^{2+}: 104; Cu^{2+}: 32	5.0	100	150–1050
Influence of stirring rate on precipitation time	Cd^{2+}: 100	5.0	30–150	495

PBD: potassium butyl dithophosphate.

1.6 Quality control

Parallel determination was performed thrice for each experimental condition, and the relative standard deviation between the samples was lower than 1%. The standard sample containing heavy metal was added to the undetermined sample, and a recovery experiment was conducted. The mean recovery of the standard addition was 99.7%.

2 Results and discussions

2.1 Structural characterization of the chelating agent

An element analyzer was used to measure four elements (C, H, O, and S) on PBD. Six PBD samples were chosen for parallel determination. The relative standard deviation of the results is lower than 1%. The measured values are compared with theoretical values (Table 2). The measured mass percentages of C, H, O, and S in synthesized PBD were very close to the theoretical value, with a relative error lower than ± 2%, indicating a high purity of the synthesized product.

The synthesized compounds were characterized by FT-IR and NMR. The stretching vibration frequencies of the compound are as follows (Lv and Zhou, 1983): CH_2 2935 cm^{-1}, P–O–C 950 cm^{-1}, 750 cm^{-1} and P=S 710 cm^{-1}, P–S 550 cm^{-1} (Fig. 1). The NMR spectrum of the compound yielded at ^1H NMR ($CDCl_3$): δ (1.52–1.61) (m, 4H, CH_2O), (3.80–3.86) (dd, 4H, CH_2) (Fig. 2a), and ^{31}P NMR ($CDCl_3$): δ 112.2 (s, 1P) (Fig. 2b). The data show major functional groups and protons of the compound are consistent with that of PBD.

2.2 Mechanism of heavy metal treatment by chelating agent

The sulfur atom in the active group of PBD has low electronegativity and a large radius. It is extremely easy to polarize and deform as well as to generate a negative electric field to capture positive ions. This characteristic of the S atom leads to bonding and production of water-insoluble butyl dithiophosphate. When the chelating agent bonds with a metal ion, a four-membered ring forms from two S atoms from each of the two chelant molecules and the metal ion.

Generally, chelating agents bond with transition metal ions to form covalently chelated products (Liu, 1982). The spatial distribution of electron-donating groups around the central ion can be determined by the distributing angle of the bonding orbital of heavy metal ions. The chelating agent can bond with heavy metals that have a valence bond orbital of dsp^2 and form a planar quadrilateral or a regular tetrahedral structure with heavy metals that have a valence bond orbital of sp^3. It can also form an octahedral structure

Table 2 Elemental analysis of PBD

	C	H	O	S
Theoretical value (% mass)	28.56	5.55	12.69	25.39
Measured value (% mass)	28.36	5.63	12.46	25.16
Relative error (%)	–0.70	1.44	–1.81	0.91

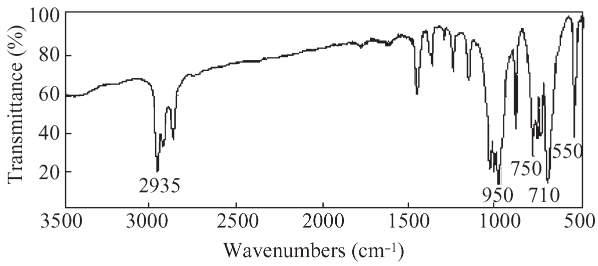


Fig. 1 FT-IR spectra of chelating agent.

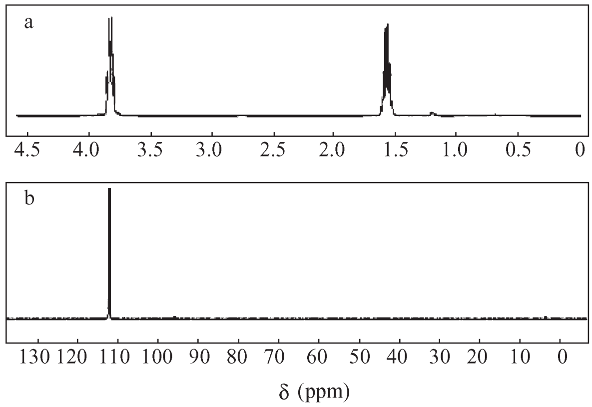
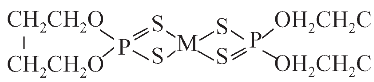


Fig. 2 NMR spectra of chelating agent. (a) 1H-NMR; (b) 31P-NMR.

with heavy metals that have a valence bond orbital of d^2sp^3. The chelating agent can bond with heavy metals in different types of valence bond orbits and form a spatial structure with low energy. Thus, the chelated products from the reaction of the chelating agent with heavy metals are stable. According to the distribution properties, outer shell electrons of Cd^{2+} coordinate with PBD in a hybrid sp^3 orbital, and the resulting structure is a regular tetrahedron. The structure of the chelated product from Cd^{2+} and PBD is as follows (Schema (3)):



(3)

2.3 Influence of pH on Cd chelation

Heavy metal wastewater is generally acidic, therefore various acid conditions were tested to analyze the influence of pH values on treatment. The chelating agent was added to wastewater containing 100 mg/L Cd^{2+} at different pH values. Figure 3 shows that when the pH is between 2 and 6, the removal of Cd^{2+} by the chelating agent does not vary considerably, and the Cd^{2+} removal rate can range from 99.92% to 99.96%. The Cd^{2+} content in the treated wastewater meets the Integrated Wastewater Discharge Standard (GB8978-1996) for Cd^{2+} (0.1 mg/L). This can be attributed to the dissociation of the chelating agent in water and the generation of butyl dithiophosphate ions with a strong coordinating capability. This helps chelate with Cd^{2+} and produce insoluble cadmium butyl dithiophosphate. As the butyl dithiophosphate ions reach dissociation equilibrium (Reaction (4)) and as it shifts rightwards following a pH increase, the concentration

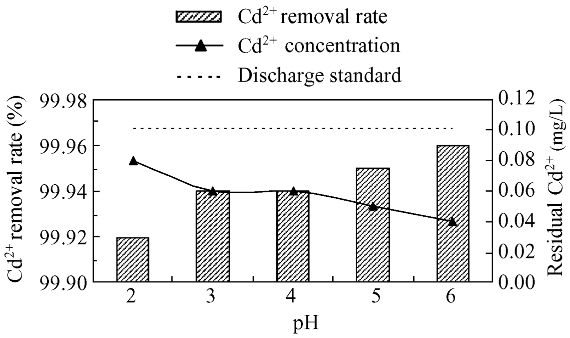
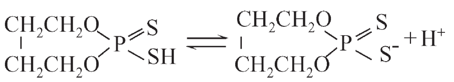


Fig. 3 Influence of pH on Cd^{2+} removal rate.

of butyl dithiophosphate ions in solution also increases and favors the production of chelated precipitates. The dissociation equilibrium of butyl dithiophosphate ions is hardly influenced by pH in the range of 2 and 6. Hence, the removal rate of Cd^{2+} is not influenced by pH within this range. Therefore, the chelating agent can be directly used to treat acid wastewater and overcome the defect in conventional precipitation with hydroxide. Without the need for pH adjustment, the method can further save on costs. For carbamate chelating-agents that are largely used in heavy metal waste treatment, the effectiveness of heavy metal removal increases with increased pH values ranging from 3 to 6, and reaches an optimum level when pH > 6 (Zhen et al., 2007). Therefore, this new PBD chelating agent has more advantages in terms of pH adaptability.



(4)

2.4 Effect of chelating agent dosage

Various PBD concentrations were added to the prepared wastewater with different Cd^{2+} concentrations at pH 5 (Fig. 4). Results suggest that there is an optimum PBD dosage for wastewater in a range of Cd^{2+} concentrations (Table 3). At a low PBD dosage, the removal rate of Cd^{2+} is slow and increases gradually as the concentration of PBD increases, reaching an optimal rate when the concentration ratio (PBD/Cd^{2+}) is between 4.95 to 5.84 (Table 3). The removal rate drops to some extent with a further increase of PBD dosage (Fig. 4). This is because PBD dissociates in water and generates a large amount of butyl dithiophosphate anions. Moreover, Cd^{2+} chelates with some of the butyl dithiophosphate ions and forms particles with

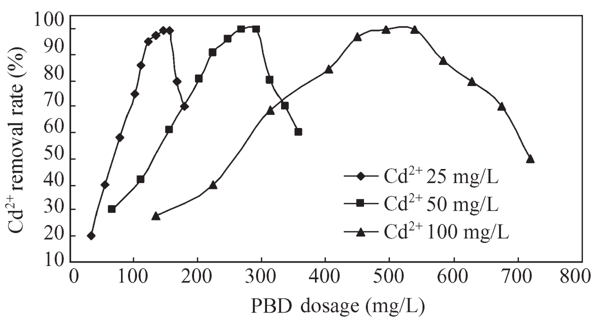


Fig. 4 Influence of chelating agent dosage on Cd^{2+} removal rate.

Table 3 Optimal dosages for wastewater with different Cd^{2+} concentrations

Cd^{2+} (mg/L)	PBD (mg/L)	PBD/Cd^{2+} (weight ratio)	Cu^{2+} removal rate (%)
25	146	5.84	99.40
50	270	5.40	99.94
100	495	4.95	99.92

negative charges because butyl dithiophosphate ions are adsorbed on their surface. Electrostatic repulsion between charged particles reduces the "bridge effect" between two chelated products and reduces settleability, thereby decreasing the removal rate (Wang and Chang, 2007). Table 3 shows that the dosage of the chelating agent required for maximal removal rate per unit amount of Cd^{2+} gradually decreases with an increase of Cd^{2+} concentration. The increase in Cd^{2+} concentration is due to the increase in the number of chelated precipitate particles. Non-reacted Cd^{2+} is adsorbed to and precipitates with the particles, reducing the required dosage of chelating agent.

2.5 Selectivity of chelating agent to heavy metal ions

Figure 5 shows the relationship of heavy metal removal rate with the chelating agent dosage in mixed wastewater, where the initial concentrations of Pb^{2+}, Cd^{2+} and Cu^{2+} are 104, 56, and 32 mg/L, respectively. If the dosage of chelating agent is insufficient, Pb^{2+}, Cd^{2+}, and Cu^{2+} ions compete for the coordination group. Pb^{2+} and Cu^{2+} form more stable chelated products than Cd^{2+} (Liu, 1982). Thus, the removal rates of Pb^{2+} and Cu^{2+} are higher than that of Cd^{2+} at low doses of the chelating agent. For example, when the dosage of PBD is 150 mg/L, the removal rates of $Cu^{2+}$and Pb^{2+} are 75% and 25%, respectively. The removal rate of Cd^{2+} is almost zero. However, when the dosage of chelating agent is sufficient (PBD: 750 mg/L), the removal rates of all the three metal ions can exceed 99%, and the dosage of the chelating agent is lower than the sum of the dosages required for Pb^{2+}, Cd^{2+} and Cu^{2+} (Table 4), because of the adsorption of free metal ions to generated precipitates. According to the solubility product rule, when precipitation induced by hydroxides is used to treat wastewater mixed with Pb^{2+}, Cd^{2+} and Cu^{2+}, the pH value should be above 10 to ensure that the Cd^{2+} concentration in treated wastewater satisfies the discharge standard. If there is plenty of OH^-,

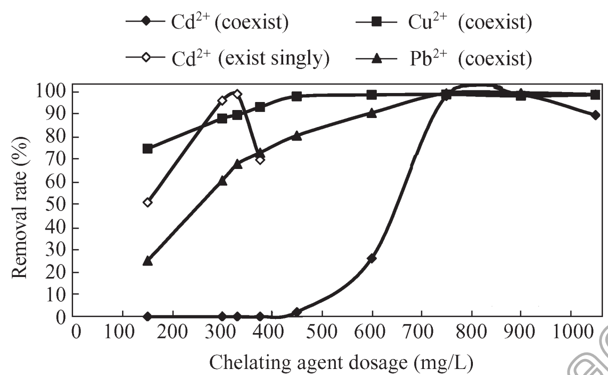


Fig. 5 Influence of co-existing heavy metal ions on Cd^{2+} removal rate.

Table 4 Optimal PBD dosages for wastewater containing different heavy metals

Metal	Initial concentration (mg/L)	PBD dosage (mg/L)	Removal rate (%)
Cd^{2+}	56	300	> 99.0
Pb^{2+}	104	290	> 99.0
Cu^{2+}	32	290	> 99.0

$Pb(OH)_2$ from metalloid Pb^{2+} is dissolved due to generated $Pb(OH)_3^-$, and a sub-sectional method has to be applied. In contrast, the chelating-precipitation method enables all the Pb^{2+}, Cd^{2+} and Cu^{2+} contents in wastewater to meet the standard through a single treatment, thereby simplifying the treatment process. The test results show that the chelating agent exhibits a weaker or stronger chelating effect with respect to different heavy metals. The sequence of chelating capabilities for the three studied heavy metal ions is: $Cu^{2+} > Pb^{2+} > Cd^{2+}$. Consequently, by controlling the dosage of the chelating agent, some heavy metal ions can be separated from other ions for reutilization.

2.6 Influence of stirring rate on precipitation time of the chelated product

Figure 6 shows the influence of the stirring rate on the precipitation time of the chelated product. The precipitation rate is faster when the stirring rate is within 90–120 r/min. A low stirring rate is unfavorable for sufficient mixing of the chelating agent and wastewater, and the precipitation time becomes relatively long due to insufficient reaction. In contrast, a stirring rate that is too high causes the flocculating constituents of the growing precipitate to fracture, and it also becomes unfavorable for rapid precipitation. Therefore, the optimal stirring rate when PBD is used to treat heavy metal wastewater is around 100 r/min, and the precipitation time of the chelated product is around 10 min.

Products chelated from Cd^{2+} and PBD settle well, and the Cd^{2+} removal rate can be above 99% after 10 min. In contrast, carbamate chelating-agents used to treat heavy metal wastewater require a coagulant to increase the precipitation rate and improve the separation effect (Wang and Hang, 2002). Therefore, when PBD is used to treat heavy metal wastewater, it has the advantages of short precipitation period and easy separation of precipitates from water.

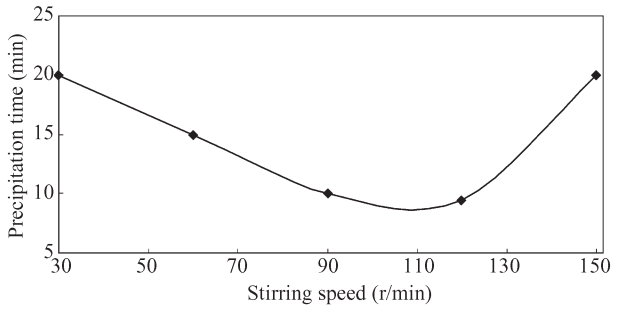


Fig. 6 Influence of agitation rate on precipitation time of the chelated product.

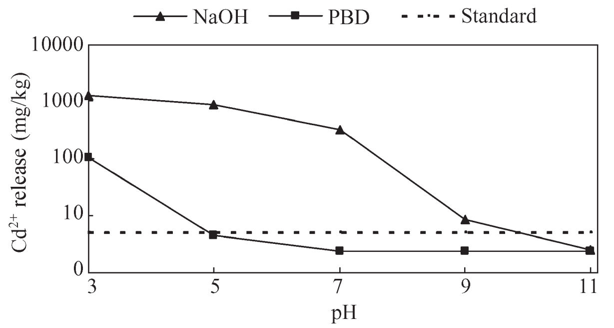


Fig. 7 Influence of pH on Cd^{2+} amount released from the chelated products.

2.7 Stability of the chelated product

Figure 7 shows the amount of Cd^{2+} leached from precipitates at different pH values when chelating agent and sodium hydroxide were used separately to treat Cd^{2+} wastewater. The amount of Cd^{2+} leached from the chelated product decreases from 100.2 to 2.3 mg/kg with increase pH values from 3 to 11. However, the amount leached from the sodium hydroxide precipitate is much higher at all pH values. For the chelated product, when pH > 5, the amount of leached Cd^{2+} can be lower than the leached amount limit specified in the Standard for Pollution Control on Security Landfill Site for Hazardous Wastes (GB18598-2001) for Cd^{2+} (5 mg/kg). When pH was 5, the amount leached from sodium hydroxide precipitate is 863 mg/kg. However, the amount leached from sodium hydroxide precipitate can meet the standard only when pH > 10. In nature, leaching gradually occurs with acidity from acid rain, causing heavy metals to be released into the aquatic environment and posing a threat to human health. The stability of chelated Cd^{2+} product is much higher than that obtained through conventional precipitation with hydroxide. Thus, when chelated products are deposited in landfills, the leakage of pollutants into the environment should be much lower than that obtained through the conventional method. Therefore, the risk of secondary pollution induced by the chelated product is low.

With the use of PBD to treat heavy metal wastewater, the water content of the chelated product after water separation is lower than 90%. A mechanical method can be used for further dehydration, and the generated sludge can be transported outside to landfills. Determination showed that the content of COD and BOD_5 generated due to residual PBD in filtrate is lower than the primary standard in the Integrated Wastewater Discharge Standard (GB8978-1996) (COD: 60mg/L, BOD_5: 20 mg/L). Thus, the filtrate can be discharged directly and will not cause environmental pollution.

3 Conclusions

Under acidic conditions, PBD chelating agents can remove 99% or more of Cd^{2+} from wastewater. The effectivity of the treatment is not influenced by pH, and the Cd^{2+} content in treated wastewater meets the Integrated Wastewater Discharge Standard (GB8978-1996). Therefore, the defect of conventional precipitation with hydroxide at an alkaline environment is overcome, and the cost for pH adjustment can be avoided. Precipitation by chelation with PBD can cause the removal not only of Cd^{2+} in wastewater, but also Pb^{2+} and Cu^{2+}. With the sequence of chelating affinity is: $Cu^{2+} > Pb^{2+} > Cd^{2+}$. By controlling the dosage of the chelating agent, heavy metal ions can be separated from other ions. The amount of Cd^{2+} leached from PBD chelates is much lower than that leached from conventional precipitates that are produced with hydroxide. When pH > 5, the concentration of leached Cd^{2+} can be lower than the limit specified in the Standard for Pollution Control on Security Landfill Site for Hazardous Wastes (GB18598-2001). Therefore, the risk of secondary pollution induced by chelated products is low.

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