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Experimental research on heavy metal wastewater treatment with dipropyl dithiophosphate

Xu Ying*, Zhang Fang

College of Environmental Science & Engineering, Hohai University, Nanjing 210098, China

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Abstract

In view of the existing technical problems about treatment of heavy metal pollution, a new organic heavy metal chelator—dipropyl dithiophosphate has been developed. This paper focuses on the mechanism about the laboratory synthesis of dipropyl dithiophosphate and chelate heavy metal, discusses the effects of pH value, added quantity of chelator, reactive time and coexistence of several heavy metal ions on the treatment effectiveness, and compares the stability of chelate complex with conventional neutral precipitation method. The results of the experiment show that, within the scope of pH 3–6, for the wastewater with the concentration of lead, cadmium, copper and mercury being 200 mg/L, dipropyl dithiophosphate enjoys a removal rate about these elements up to over 99.9%, and the concentrations of the lead, cadmium, copper and mercury in the wastewater after treatment are less than 1, 0.1, 0.5 and 0.05 mg/L, respectively, which meet the limit value of concentration stipulated in the *Integrated Wastewater Discharge Standard* (GB8978-1996). And the treatment effectiveness are not affected by pH value and coexistent heavy metal ions, which makes up the deficiency that neutral precipitation must be used under the condition of high alkalinity. The optimum quantity of dipropyl dithiophosphate chelator added is 1.2 times as much as stoichiometric amount and the optimum reactive time is 20 min for lead, cadmium and copper, and 30 min for mercury. Within the scope of pH 3–9, each heavy metal ion release of chelate complex will decrease along with increased pH value. But under any pH conditions, the release of heavy metal ions in hydroxide is far higher than that in chelate complex, therefore reducing the risk of polluting the environment again.

Keywords: Heavy metal; Chelate precipitation; Wastewater treatment; Lead; Cadmium; Copper; Mercury

1. Introduction

The industries such as mine, metallurgy, machine manufacturing, chemical industry, electronics and instrument, etc., produce large quantities of heavy metal wastewater every year, part of which is poured into water bodies without treatment or standard treatment, which results in the pollution of the aquatic environment. Because heavy metals are difficult to be biodegraded and ruined in natural conditions, they are usually ingested by aquatic animals and plants, as well as the crops on the land, and then enter into human body through food chain after high enrichment in the propagation's bodies. They accumulate in some organs of human body and cause the chronic intoxication, which seriously endangers the health of human body. The world-shaking "Minamata disease" and "Itai-itai disease" are just caused by environmental pollution with wastewater containing mercury and cadmium, respectively. Therefore, heavy metal wastewater is a kind of industrial wastewater which seriously pollutes the environment and endangers human being.

Different kinds of heavy metals exist in the solution with different forms, so their treatment methods are also different. As for the treatment of heavy metal wastewater, many methods have been put forward at home and abroad, including chemical-treatment method, ion-exchange method, electrolytic method, adsorption method, reverse-osmosis method, electrodialytic method, evaporating concentration and biological treatment, etc. However, limited by economic and technical reasons, the method mostly adopted at home and abroad for the treatment of heavy metal currently is the chemical method of neutral precipitation. But it has been proved by the application practice that the following problems are present in neutral precipitation method [1]: (1) heavy metal wastewater generally appears acidic, which should not be drained out until neutral treatment with

* Corresponding author.
E-mail address: xyhohai@163.com (X. Ying).

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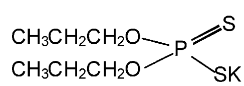
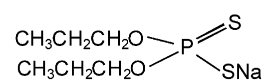
controlling its pH value over 10 by means of neutral precipitation method; (2) when amphoteric metals, such as zinc, lead, tin and aluminum, etc., coexist in the wastewater, along with the raise of waste-water pH value, the amphoteric metals will appear the tendency of redissolving. So it is a must to control the pH value strictly and carry out fractional precipitation; (3) some metal ions can form very stable complex compounds together with the halogen, cyanogen roots and humic substance and so on in waste water. For the complex compounds are very difficult to be removed with the method of neutral precipitation, it is necessary to carry out pretreatment about the wastewater; (4) precipitation of hydroxide produced by heavy metal ions in the alkali medium will strip again along with the lowering of pH value, which causes secondary pollution. Therefore, with the increasingly complicated compositions of heavy metal wastewater, the requirements on wastewater discharge have gradually become stricter. And the conventional neutral precipitation method cannot meet the treatment requirements any longer [2].

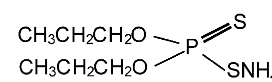
The research adopted the organic chelator to treat heavy metal has been started internationally [3,4] in consideration of the existing problems in the pollution treatment technology of heavy metal. This type of chelator can combine with heavy metal ion through coordinate link to form stable insoluble chelate complex, so as to eventually remove heavy metal. The most heavy metal chelators being studied currently are dithiocarbamate and its ramifications. And this method has got a preliminary application in heavy metal wastewater treatment as well as solidification of incinerator fly ash and heavy metal in Japan [5–8]. pH value for application of dithiocarbamate and its ramifications is 6–8, while heavy metal wastewater usually appears acidic, so the problem of increased treatment cost due to pH adjustment still exists. If this type of chelator is used in acidic wastewater, poisonous gases will be generated and cause secondary pollution to the environment. Besides, this type of chelator has complex synthetic process and consumes relatively plentiful raw materials, so the cost for the synthesis of chelators is relatively high. In recent years, the chelators newly studied still include pyridine-thiol and 1,3-benzenediamidoethanethiol, and the later one has already been applied to the treatment of acidic mine wastewater [9]. The experimental results [10,11] show that the reaction speed of the two chelators with metallic ions is relatively slow. To treat wastewater containing 50 ppm Cd^{2+} and Cu^{2+}, respectively, with pyridine-thiol and reach a removal rate of over 99%, the necessary reaction time is 1 and 4 h, respectively. And even to treat wastewater containing 50 ppm Pb^{2+} and Hg^{2+} with 1,3-benzenediamidoethanethiol, respectively, then 1 h is also required for each reaction to reach a removal rate of over 99%. The increased reaction time will surely induce increased investment cost for treatment facilities. Based on related domestic and overseas research, the authors have developed a new type of organic heavy metal chelator, that is dipropyl dithiophosphate. Compared with dithiocarbamate and its ramifications, dipropyl dithiophosphate chelator can be used to treat acidic wastewater with reduced risks of generating poisonous gases due to different molecular structures of the two types of chelators, so it has more advantages in terms of the applicable scope of pH value. Compared with pyridine-thiol and 1,3-benzenediamidoethanethiol, dipropyl dithiophosphate can reduce the investment cost for treatment facilities for its extremely strong combining capacity with metallic ions, quick reaction speed, about 30 min stirring reaction and removal rate of over 99% to each metallic ion. In addition, dipropyl dithiophosphate is made from phosphorus pentasulfide and monohydric alcohol in alkali or ammonia. The synthetic process is very simple and the raw materials are relatively cheap, so the price of this chelator is relatively low. The structural formula of dipropyl dithiophosphate is as follows:



PDD

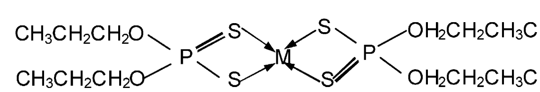


SDD



ADD

Potassium dipropyl dithiophosphate, sodium dipropyl dithiophosphate and ammonium dipropyl dithiophosphate are denoted with abbreviations PDD, SDD and ADD, respectively. The sulfur atom in the active group of dipropyl dithiophosphate chelator has small electronegativity and big semi-diameter, and is extremely easy to lose electrons, polarize and deform, eventually producing negative electronic field. When the chelator combines with a certain metallic ion, the two sulfur atoms in its structure and the metal ion will make chelate precipitation with the following structure:



The reaction equation of dipropyl dithiophosphate and heavy metal is (take potassium dipropyl dithiophosphate as an example):

$$2C_6H_{14}O_2PS_2K + M^{2+} \rightarrow C_{12}H_{28}O_4P_2S_4M \downarrow + 2K^+$$

In the equation, M^{2+} stands for the divalent metal ion, such as lead, cadmium, copper, mercury, etc. The chelator and the metal ion form covalent chelate complex. The space adaption of the electron donating groups around the central ion are subject to the angles of the adaption of metallic ion bonding orbital. For the space structure with relatively small tension formed by the chelator and metallic ions with different valence bond orbital [12], the chelate complex produced by the reaction of the chelator and metallic ions have relatively high stability. In this paper discusses the influencing factors of applying dipropyl dithiophosphate to treating the wastewater containing lead, cadmium, copper and mercury as well as the stability of chelate complex, which provides theoretical and practical basis for the application of chelator.

2. Materials and methods

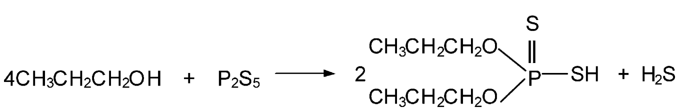
2.1. Materials

Apply P_2S_5, $CH_3CH_2CH_2OH$, K_2CO_3, Na_2CO_3 and $NH_3{\cdot}H_2O$ to synthesizing chelator. P_2S_5 is chemically pure reagent, and $CH_3CH_2CH_2OH$, K_2CO_3, Na_2CO_3, are analytical reagents (AR). Adopt analytic reagent such as $pb(NO_3)_2$, $CdCl_2{\cdot}2.5H_2O$, $Cu(NO_3)_2{\cdot}3H_2O$, and $HgCl_2$ to compound wastewater containing lead, cadmium, copper and mercury. And make use of guaranteed reagents such as NaOH and HNO_3 to adjust the pH value of the wastewater. All the materials above are bought from the shop of chemical reagents. The standard liquid of lead, cadmium, copper and mercury used in concentration analysis of the heavy metals in wastewater is bought from China National Environmental Monitoring Center.

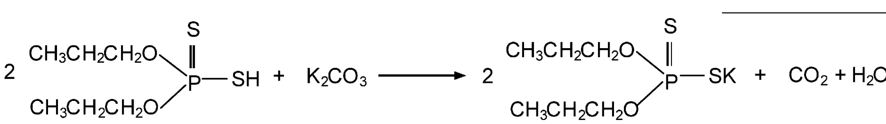
2.2. Methods

2.2.1. Synthesis of chelator

P_2S_5 and $CH_3CH_2CH_2OH$ react and produce diopropyl phosphonodithioate, as shown in the reaction equation:



Then, respectively, use K_2CO_3, Na_2CO_3 and $NH_3{\cdot}H_2O$ to react with dipropyl phosphorodithioate to produce potassium dipropyl dithiophosphate, sodium dipropyl dithiophosphate and ammonium dipropyl dithiophosphate, as shown in the reaction equation (take potassium dipropyl dithiophosphat as an example):



2.2.2. Infrared detection of chelator

The existence of the main functional group in chelators has been proved by checking and measuring the synthetic chelators potassium dipropyl dithiophosphate, sodium dipropyl dithiophosphate and ammonium dipropyl dithiophosphate with infrared spectrophotometer, and through the contrast analysis of experimental infrared spectra and standard infrared spectra. As for the checking and measuring data of chelators with infrared spectrophotometer, please see Table 1.

Table 2
Chelator bio-toxicity data

Name of chelator	24 h-IC_{50} (g/L)	7 day-MATC (g/L)
Potassium dipropyl dithiophosphate	270	35.5
Sodium dipropyl dithiophosphate	300	39.8
Ammonium dipropyl dithiophosphate	81.3	13.3

2.2.3. Bio-toxicity detection of chelator

The experiment of 24 h acute toxicity and 7 day chronic toxicity, with the mixed bacterium in the river as the tested organism and adoption of the growth inhibition measurement method, is carried out for potassium dipropyl dithiophosphate, sodium dipropyl dithiophosphate and ammonium dipropyl dithiophosphate. Two results are obtained: the chelator concentration (IC_{50}) when 50% of the river bacteria activity is restrained and the maximum acceptable toxicant concentration (MATC) of chelator to the river bacteria. The results are shown in Table 2. When chelator is adopted in the waterwaste treatment processing of heavy metal, its concentration in the waterwaste effluent is greatly less than the maximum acceptable toxicant concentration of chelator to the river bacteria, so the application of these three chelators will not cause secondary pollution to the environment.

2.2.4. Experiment of effects on treatment effectiveness

(1) Respectively, prepare the wastewater of lead, cadmium, copper and mercury being 200 mg/L, and get samples of 50 mL in the small beaker. Control pH value of wastewater, added quantity of chelator and reactive time. Filter them after stiring the samples with magnetic stirring apparatus and keeping them static, and then measure the ion concentration of heavy metals in the filtrate, watching how reactive time, pH value and the added quantity of chelator affect the treatment effectiveness.

(2) Prepare the wastewater with lead, cadmium, copper and mercury concentration, respectively, being 200 mg/L, as well as

Table 1
The stretching vibration frequency of the main functional groups in chelators

Name of chelator	P=S (cm^{-1})	P–S (cm^{-1})	P–O–C (cm^{-1})	NH_4^+ (cm^{-1})	CH (cm^{-1})
Potassium dipropyl dithiophosphate	710	552	748 992		2967
Sodium dipropyl dithiophosphate	673	559	762 940		2976
Ammonium dipropyl dithiophosphate	669	545	800 975	3143	2965

the composite waste with the lead, cadmium, copper and mercury concentration being 200 mg/L. Get the water samples of 50 mL in the small beakers, set up their pH value, reactive time and control the added quantity of chelator. Filter them after stirring the samples with magnetic stirring apparatus and keeping them static. Then measure the ion concentration of heavy metals in the filtrate and observe the removal results of each heavy metal ion while lead, cadmium, copper and mercury exist separately as well as coexist under the circumstance that the added quantity of the chelator is the same.

2.2.5. *Stability experiment of chelator complex*

After being desiccated at 40 °C, the precipiates produced by potassium dipropyl dithiophosphate, sodium dipropyl dithiophosphate, ammonium dipropyl dithiophosphate and NaOH, respectively, reacting with lead, cadmium, copper and mercury are, respectively, put into the liquids whose pH values are 3, 5, 7 and 9. Set the weight ratio of liquid to solid as 10. Filter them after stirring 6 h and measure the concentration of lead, cadmium, copper and mercury in the liquid. Observe release changes of heavy metal ions in the chelate complex under the circumstance of different pH value. The method can be used to evaluate the stability of chelate complex under different environmental conditions [13].

2.2.6. *Analytic methods*

The concentrations of lead, cadmium and copper in the samples are measured by TAS-986 atomic absorption spectrophotometer, and the concentration of mercury by AFS-830 atomic fluorescence spectrophotometer. Please refer to GB7485-87 for the analytic method against lead, GB7475-87 for the analytic method against cadmium and copper, and GB7468-87 against mercury. Carry out repeated experiment thrice under each experimental condition with the standard deviation of experimental results within 1%. Then adopt the average value of the experimental results to discuss the influential factors when treating wastewater containing lead, cadmium, copper and mercury with dipropyl dithiophosphate and the stability of the chelate complex produced.

3. Results and discussion

3.1. *Effects of the reactive time on treatment effectiveness*

The experiment, concerning the influence of reaction time on treatment effectiveness, is carried out under the conditions that the pH value is 5.0 and the quantity of dipropyl dithiophosphate added is 1.2 times as much as the theoretical quantity added (stoichiometric amount). Fig. 1 shows that after 10 min, the concentration of lead, cadmium, copper and mercury is reduced from 200 mg/L to less than 4.0 mg/L, respetively, and the removal rates is over 98%. The leaving concentration of lead, cadmium and copper after 20 min of reaction and that of mercury after 30 min of reaction are under the concentration limit value stipulated in *Integrated Wastewater Discharge Standard* (GB8978-1996) (Pb, 1 mg/L; Cd, 0.1 mg/L; Cu, 0.5 mg/L; Hg, 0.05 mg/L). The removal rate of all the metal ions is more than 99.9%. Therefore, we can choose proper reactive time according to the treatment requirements.

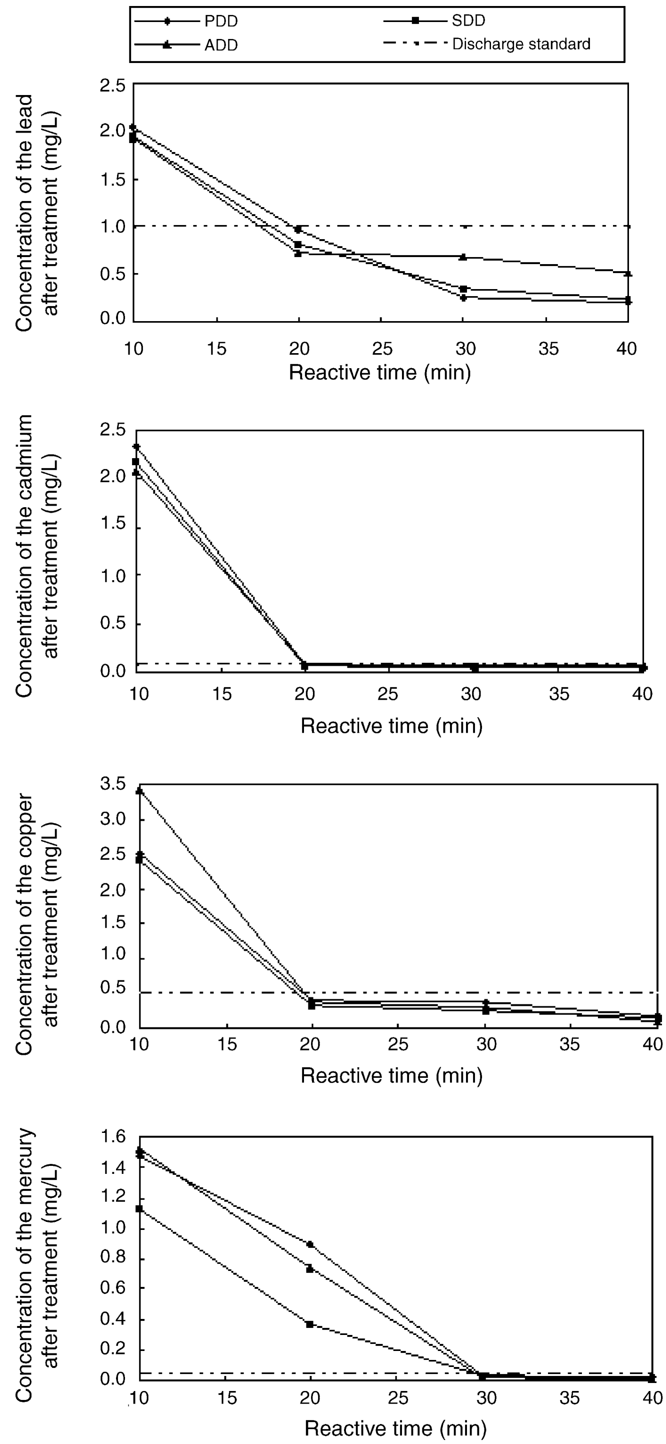


Fig. 1. Effects caused by the reactive time on treatment effectiveness.

3.2. *Effects caused by the added quantity of chelator on treatment effectiveness*

The experiment, concerning the influence of the quantity of chelator added on treatment effectiveness, is carried out under the conditions that pH value is 5.0 and the reaction time of

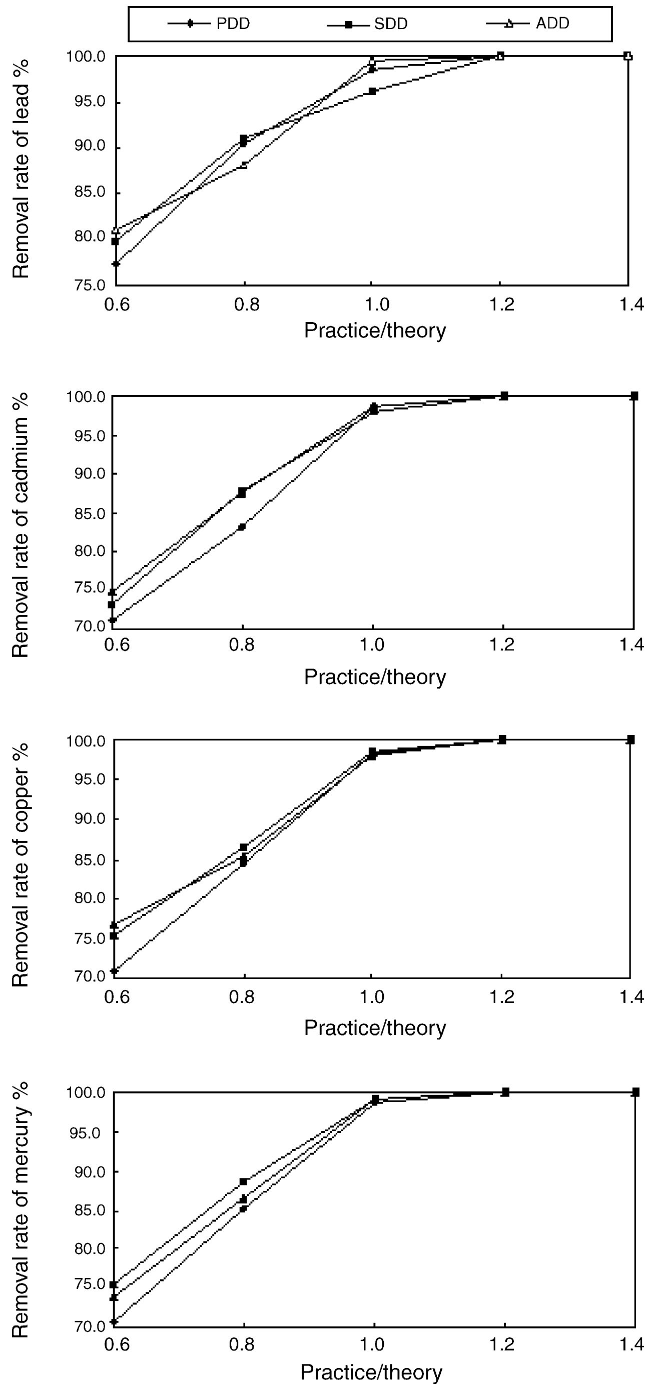


Fig. 2. Effects caused by the added quantity of chelator on treatment effectiveness.

dipropyl dithiophosphate with lead, cadmium, copper and mercury is 30 min. Fig. 2 shows that the removal rates of lead, cadmium, copper and mercury by the three chelators increase with the increasing quantity of chelators added, especially rapidly increase before reaching stoichiometric point. When reaching the point, the removal rates of each metal ion by the chelator will exceed 98%, and if the quantity of chelator added is 1.2 times of the stoichiometric amount, the removal rates will exceed 99.9%, which has met the national discharge standard (GB8978-1996) of lead, cadmium, copper and mercury content in the wastewater. If we continue to add the chelator, the increase of the removal rates becomes very slow. So it is better to add chelator which is 1.2 times of stoichiometric amount.

3.3. Effects caused by pH value on treatment effectiveness

Carry out the experiment concerning the influence of pH value on treatment effectiveness under the conditions that the quantity of dipropyl dithiophosphate added is 1.2 times as much as the theoretical quantity added (stoichiometric amount) and the reaction time is 30 min. According to the analysis of Fig. 3, we can see that in the scope of pH 3–6, removal rates of lead, cadmium, copper and mercury by the three chelators are all more than 99.9%, and contents of lead, cadmium, copper and mercury in the wastewater meet the national discharge standard (GB8978-1996). Therefore, the chelator can be used directly

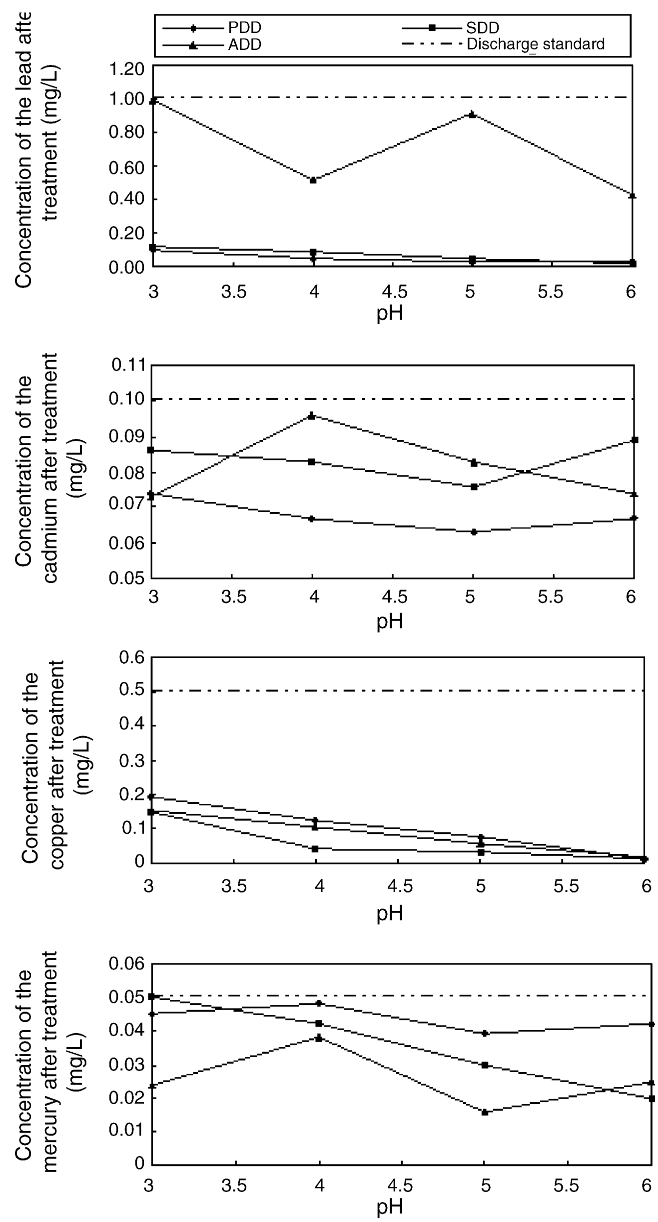


Fig. 3. Effects caused by pH value on treatment effectiveness.

for acid heavy metal wastewater treatment, which makes up for the weakness that conventional neutral precipitation method has under acid conditions, saving the expenses of adjusting acid salt tolerance.

3.4. Effects caused by the coexistence of metal ions on treatment effectiveness

Fig. 4 indicates the changes of removal rates of heavy metals with the change of added quantity of potassium dipropyl dithiophosphat in the composite waste containing lead, cadmium, copper and mercury, respectively, as well as the wastewater, respectively, containing the lead, cadmium, copper and mercury. In the experiment, the pH value of the wastewater controlled is 5 with the reaction time 30 min.The analyses of experiment results show that when the ratios between practical add-on and theoretical add-on are 0.6 and 0.8, respectively, the ions of lead, cadmium, copper and mercury compete for dentate. And because the chelate complex composed by lead, copper and chelator has a relatively high stability and occupies the dentate firstly, the removal rates of lead and copper in the composite waste are higher than the removal rates of these metal ions in the wastewater with single one. While removal rate of cadmium and mercury is very low for the lack of dentate, especially when the ratio between practical add-on and theoretical add-on of is 0.6, the removal rate of cadimium even approximates to zero. When the ratios between practical add-on and theoretical add-on are 1.0, the adequate dentate and adsorption of the produced precipitate to metal ions make the removal rate of the four metal ions over 99.9%, which is higher than that of the metal ions when they exist separately. If we resort to the method of precipitation of hydroxide, the pH values of cadmium, copper and mercury should be more than 10. Because lead is amphoteric metal, under this circumstance, lead hydroxide will dissolve and exceed the standard, and the treatment of wasterwater should be conducted by stages. But the chelate precipitation can make content of lead, cadmium, copper and mercury in the wastewater meet the standard (GB8978-1996) by one-time wastewater treatment, thus, it may simplify the treatment process.

3.5. Stability of chelator complex

Fig. 5 displays release changes of heavy metal ions in the precipitates with the change of pH value during the course of processing the wastewater containing lead, cadmium, copper and mercury with the dipropyl dithiophosphate and NaOH. The experiment results show when pH value is 3–9, the release of heavy metal ions in chelate complex reduces with the increase of pH value. But whatever the pH value is, the release of heavy metal ions in hydroxide is much higher than that in chelate complex. Among these, the difference of lead release is particularly evident. We can draw a conclusion from this that the stability of chelate complex composed by dipropyl dithiophosphate together with heavy metal ions is much higher than that produced in neutral precipitation, which reduces the risks of polluting the environment by chelate complex. The stability order of chelate complex composed by dipropyl dithiophosphate with lead, cadmium, copper and mercury is: copper > lead > mercury > cadmium. Because the stability of the chelate complex mentioned above reduces with the increase of the metal alkalescence, chelate complex produced by weakly alkalescent copper is the most stable, and comparatively the chelate complex produced by cadmium is the least stable.

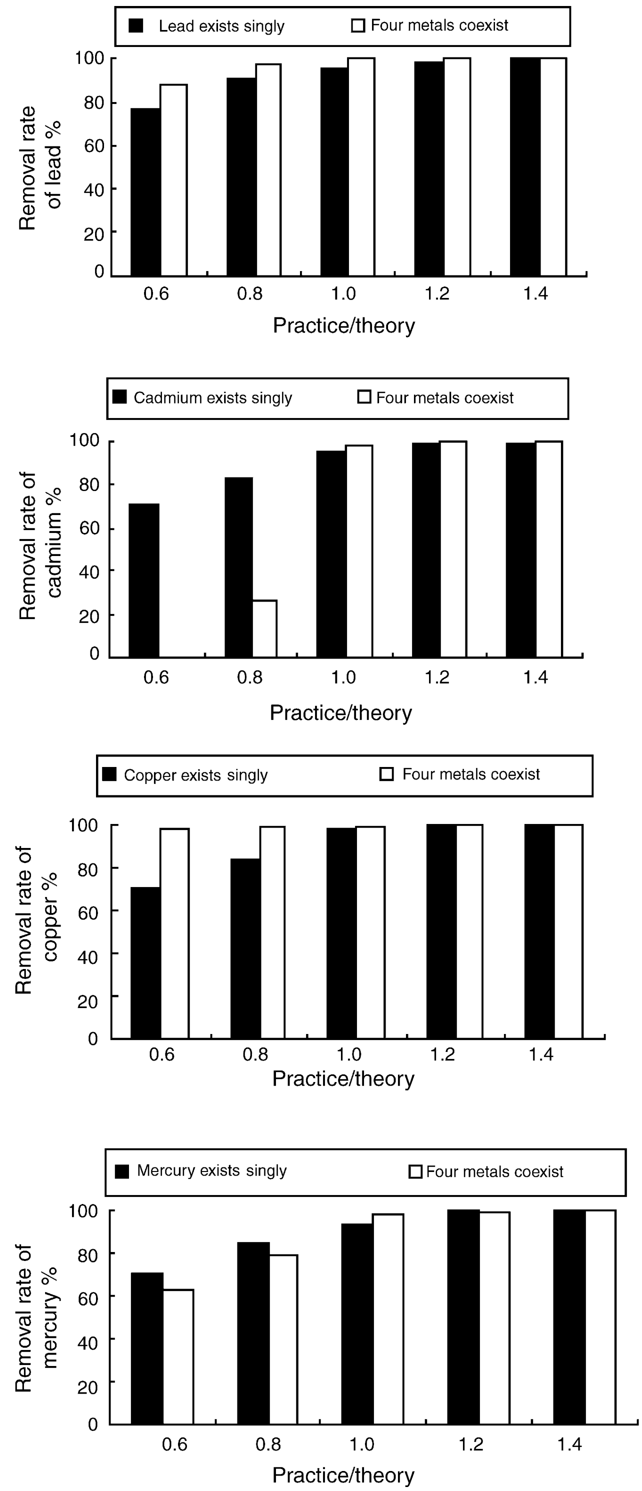


Fig. 4. Effects caused by the coexistence of metal ions on treatment effectiveness.

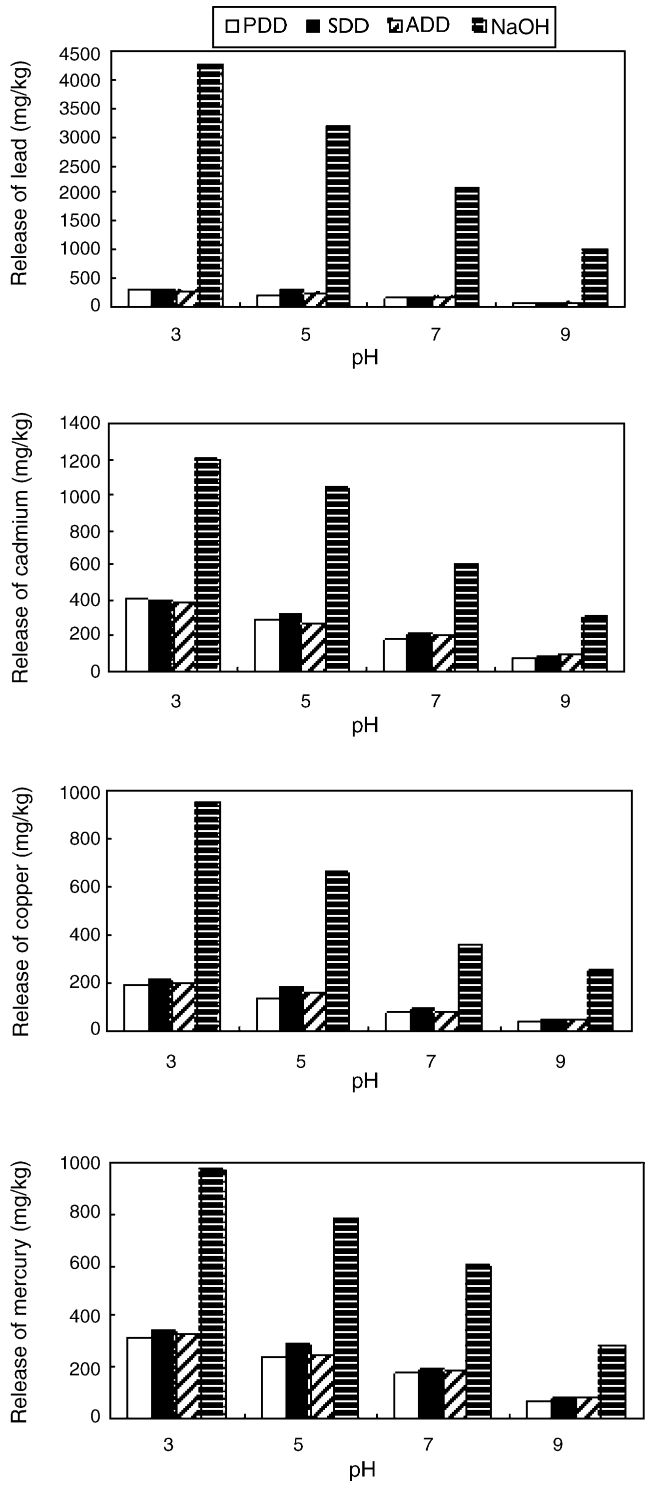


Fig. 5. Effects caused by pH value on heavy metal release of chelate complex.

4. Conclusion

The removal rates of lead, cadmium, copper and mercury by dipropyl dithiophosphate chelator under acid conditions can be more than 99.9%. The treatment effectiveness do not affected by pH value and the coexistence of several heavy metal ions. Contents of lead, cadmium, copper and mercury in the wastewater after treatment satisfy the concentration limit stipulated in *Integrated Wastewater Discharge Standard* (GB8978-1996), which makes up the weakness that neutral precipitation has under the high alkalinity circumstance, and saves the expenses of adjusting acid salt tolerance. The optimum added quantity of dipropyl dithiophosphate chelator is 1.2 times as much as stoichiometric amount and the optimum reactive time is 20 min for lead, cadmium and copper, and 30 min for mercury. The stability of chelate complex made by dipropyl dithiophosphate together with lead, cadmium, copper and mercury is much higher than the precipitates produced in neutral precipitation, which reduces the risks of polluting the environment by chelate complex. Compared with such chelators as ithiocarbamate and its ramifications, pyridine-thiol and 1,3-benzenediamidoethanethiol, dipropyl dithiophosphate chelator has more advantages in terms of applicable pH scope, reaction time and treatment cost, etc. The dipropyl dithiophosphate chelate precipitation is a new way to carry out chemical treatment of heavy metal ions, and also break a new study field about the precipitate theory of wastewater treatment. This method excels the conventional method of chemical treatment, showing certain prospect of spread and application.

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