Comparative investigation of *N,N′*-bis-(dithiocarboxy)piperazine and diethyldithiocarbamate as precipitants for Ni(II) in simulated wastewater

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Abstract

The performances of a coordination polymerization precipitant, *N,N′*-bis-(dithiocarboxy)piperazine (BDP) were compared with the widely used heavy metal precipitant, diethyldithiocarbamate (DDTC), through the treatment of three kinds of nickel-containing wastewaters, $NiSO_4$, nickel citrate (NiCA) and Ni^{2+}-dye. Results indicated that both BDP and DDTC at their stiochiometric doses could reduce $50.00\,mg\,l^{-1}$ free nickel(II) to lower than $1.0\,mg\,l^{-1}$ (discharge limit of nickel ions in China) and 10% precipitants doses increase could treat NiCA containing $50.00\,mg\,l^{-1}$ Ni^{2+} to meet the discharge limit. But $[NiBDP]_n$ coordination polymerization precipitates had more rapid settling speed than $Ni(DDTC)_2$ precipitates. It was also observed that BDP could still partly remove Reactive Brilliant Red X-3B from Ni(II)-dye integrated wastewater through the adsorption of the precipitates $[NiBDP]_n$, in addition to precipitating Ni(II). A 1:1 stiochiometric dose of BDP/Ni(II) could decrease Ni(II) from 50.00 to $0.87\,mg\,l^{-1}$, and simultaneously reduce the dye from 30.00 to $19.52\,mg\,l^{-1}$.
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Keywords: Nickel wastewater; Precipitant; Coordination polymerization precipitation

1. Introduction

Nickel is a transition metal that is generally considered to be an essential micronutrient but its excess is detrimental to the health of organic bodies when exposed in the environment [1,2]. Its maximum contaminant limit in potable water has been fixed as $20\,\mu g\,l^{-1}$ by the European Communities [3]. However, many wastewaters discharged from electroplating and metal cleaning, especially electronics industries often contain high concentrations of nickel ions [4]. Therefore, the removal of Ni(II) in the wastewater has received considerable attention in the past years.

To remove Ni(II) from wastewaters, a number of treatment technologies such as chemical precipitation [5–7], ion exchange [8,9] and adsorption [10,11], etc. have been used in recent years. Most of these methods involve high cost and are only suitable for small-scale industries, while the chemical precipitation is widely applied due to its simple equipments, convenient operation, capability to treat large volume of water containing heavy metals, low cost and so on [12]. Dithiocarbamate is one of the most widely used commercial chemical precipitants. It is often marketed in two forms, sodium dimethyldithiocarbamate and diethyldithiocarbamate (DDTC) [13]. It is noted that DDTC only provides single chelating group each molecular and its reaction with nickel ions only forms simple chelating precipitates (Fig. 1a), rather than coordination polymerization precipitates. Generally, coordination polymerization precipitates possess more favorable settling performance. Therefore, it is of great research interest for wastewater treatment to develop chelating precipitants with multiple chelating groups and with the ability to form stable coordination polymerization precipitates with Ni ions. However, to date there is no concerning report. This situation encourages us to probe the application of the chelating agents with multiple chelating groups to remove Ni(II) from wastewaters by the formation of coordination polymerization precipitates. The treatment process was referred to as coordination polymerization precipitation (CPP) in this paper.

In our previous work, a two-dithiocarboxy-group compound, disodium *N,N′*-bis-(dithiocarboxy)piperazine (Na_2BDP) (Fig. 1b), was used as a CPP precipitant for Cu^{2+} [14]. In this paper we will continue to investigate the performances of
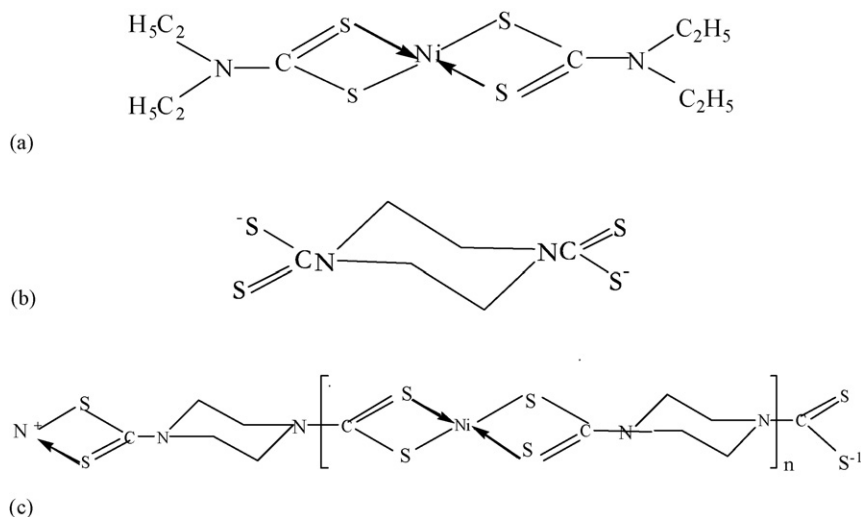

Fig. 1. (a) Structure of Ni(DDTC)$_2$; (b) structure of BDP; (c) structure of [NiBDP]$_n$.

BDP as a CPP precipitant for Ni^{2+} ions. The piperazine ring in BDP offers a stiff building block to separate the two dithiocarboxy groups on both ends of the ring so that they are forced to respectively bind different metal ions [15,16]. Therefore, it was expected that two dithiocarboxy groups of two different BDP molecules could bridge Ni^{2+} centers to yield a large insoluble linear coordination polymerization precipitate [NiBDP]$_n$, as presented in Fig. 1c.

In this paper, Na$_2$BDP was employed to treat three kinds of Ni(II)-containing wastewaters, NiSO$_4$, nickel citrate (NiCA) and NiSO$_4$-dye, which were selected as the representations of free Ni(II), coordinated Ni(II) and integrated simulated wastewater, respectively. This work has the following basic objectives: (1) to investigate the feasibility of applying BDP as a CPP precipitant to the treatment of Ni(II)-containing wastewater; (2) to compare the performances of the CPP precipitant, BDP, versus the widely used heavy metal precipitant, DDTC, in the process of Ni(II) removal from the wastewaters.

2. Materials and methods

2.1. Materials

Anhydrous piperazine (≥99%) was from Changzhou Shanfeng chemical company. And Reactive Brilliant Red X-3B (X-

3B) (Fig. 2) (98% purity) was obtained from China dyestuff chemicals and used directly without further purification. The other reagents used in the experiment were of analytical grade.

2.2. Analytical apparatus and methods

Elemental analyses were performenced on a Vario Elementar. The concentrations of nickel(II) in the solution were determined using the colorimetric nickel(II) reagent dimethylgloxime according to the reported method [17] on a UV-PC 3101PC spectrophotometer (Shimaszu, Japan). Turbidity of solutions was measured with a UV-PC spectrophotometer at 680 nm, and the pH values of solutions were determined using PHS-3C pH meter.

2.3. Synthesis of Na$_2$BDP·6H$_2$O

The CPP precipitant Na$_2$BDP·6H$_2$O was synthesized by the reaction of piperazine with CS$_2$ and NaOH in dry ethyl ether and isopropyl alcohol under vigorous stirring over 5 h [18]. Initial molar ratios of piperazine, CS$_2$ and NaOH were 1:2:2. The crude product was re-crystallized from methanol–water mixture. Elemental analyses of Na$_2$BDP·6H$_2$O found were C: 18.67, H: 5.39, N: 7.15, S: 32.50; (calculated) C: 18.46, H: 5.16, N: 7.17, S: 32.85.

2.4. Process of Ni(II) removal

Add a definite dose of BDP or DDTC to 50 ml NiSO$_4$ or NiCA or NiSO$_4$ X-3B aqueous solutions containing 50.00 mg l^{-1} Ni(II), respectively, and then agitate for 5 min at a speed of 85 rpm. The residual Ni(II) concentrations in the solutions were analyzed using a UV-PC spectrophotometer at the wavelength of 530 nm after filtration by qualitative filter paper. All experiments were carried out at room temperature (25 ± 1 °C) and under normal atmospheric conditions.
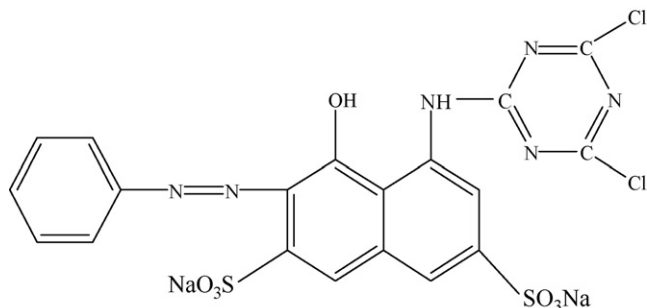

Fig. 2. Structure of Reactive Brilliant Red X-3B (X-3B).

2.5. Isothermal adsorption

The isothermal adsorption of X-3B on nickel precipitates was conducted in 100 ml flasks. The experimental procedure was as follows: after stoichiometric dosages of BDP or DDTC were mixed with 50 ml solution containing 50 mg l^{-1} Ni(II), various concentrations of X-3B were added in the resulting suspensions and then equilibrated at $25 \pm 1\,^{\circ}$C for 4 h. All adsorption experiments were carried out at initial pH 7.0. After equilibration, the resulting suspensions were centrifuged and the X-3B concentrations in the solution were determined using the UV–vis spectrometer at 536 nm, the maximum absorption wavelength of the dye. These UV–vis data were used to calculate the adsorption capacity, q_e of the adsorbent, [NiBDP]$_n$ or Ni(DDTC)$_2$ precipitates. The adsorption capacity q_e given in mg g^{-1} was calculated from the following equation:

$$q_e = \frac{(C_0 - C_e)V}{m_s} \tag{1}$$

where C_0 and C_e are the initial and final X-3B concentrations in solution (mg l^{-1}), V the solution volume (l), and m_s is the mass of precipitate (g).

3. Results and discussion

3.1. Removal of free nickel(II)

As BDP was mixed with NiSO$_4$ solution, a lot of small green precipitates generated immediately. In the process of subsequent 5 min agitation, these small precipitates gradually aggregated into big floccules and subsided from the solution. As DDTC was added in NiSO$_4$ solution, the solution instantly turned to olivine but no precipitate was observed. Even after agitating for 5 min, only part of precipitates slowly subsided from the solution and many small precipitates were still suspended in the solution. In order to confirm the chemical stoichiometry of the precipitation reaction of BDP and Ni(II), the concentrations of residual Ni(II) in the filtrate of the above resulting solutions were determined. As shown in Fig. 3a, the residual nickel ions were decreased sharply with the increase of BDP. At 1:1 stoichiometry, the residual nickel concentration was 0.10 mg l^{-1}, which was far below the discharge limit of nickel in China, 1.0 mg l^{-1}. The inflexion of the curve appears at 1:1 molar ratio, confirming that the reaction product of BDP and Ni^{2+} was a polymer precipitate with a 1:1 stoichiometry, as presented in Fig. 1c. The stoichiometry is consistent with the reported formula in the papers by Aravindakshan [19,20]. Comparatively, the residual concentration of Ni(II) was slowly reduced with the increase of DDTC. Its inflexion was at 2:1 molar ratio of DDTC/Ni^{2+} and at this molar ratio the residual nickel concentration was 0.76 mg l^{-1}.

The effect of initial pH value on the residual Ni^{2+} concentrations is depicted in Fig. 4a. From the figure, it can be seen that the increase of pH value is beneficial to nickel(II) removal and the pH possesses a rather similar effect on the removal of Ni(II) by BDP and DDTC. The inflexions of the two curves both appear at pH 7 and their corresponding concentrations of the residual
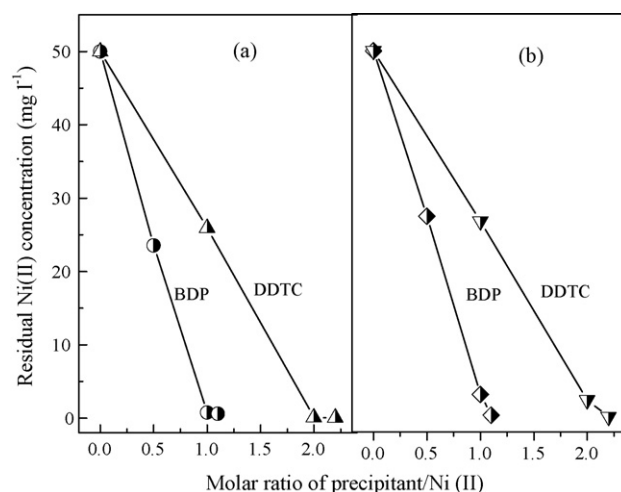

Fig. 3. Dependence of residual Ni^{2+} concentration on the molar ratio of BDP/Ni(II) and DDTC/Ni(II) with an initial pH of 7.0: (a) NiSO$_4$ containing 50.00 mg l^{-1} Ni^{2+}; (b) NiCA containing 50.00 mg l^{-1} Ni(II).

Ni(II) are both lower than the discharge limit of nickel ion in China. Therefore, both BDP and DDTC can be applied over pH 7.

The above experimental data were obtained from the filtrates, however, in practical application a solid–liquid separation is generally carried by a sedimentation process, not by filtration. Therefore, the settling performances of [NiBDP]$_n$ and Ni(DDTC)$_2$ precipitates were also investigated. The experimental results showed the two precipitates possessed different settling behaviors. From Fig. 5a, after 5 min agitation following 1 min settling, the residual turbidity of the solution treated by BDP is only seven NTU while that of the solution treated by DDTC is as high as 93 NTU. Even after 1 h settling, the solution still remains a turbidity of 60 NTU. This fact indicated that BDP coordination polymerization precipitates had much more rapid settling speed than DDTC precipitates.
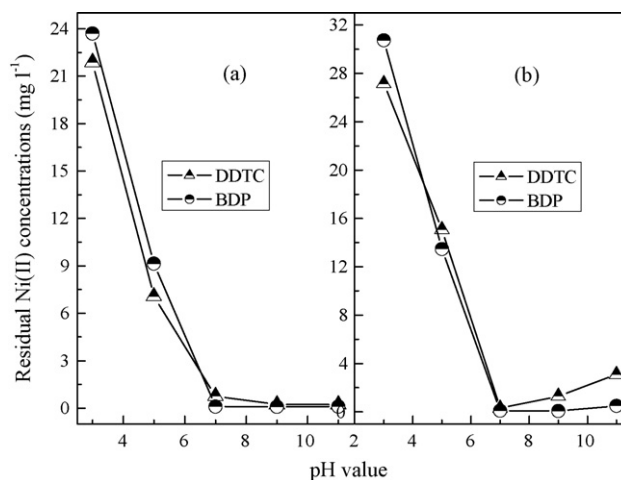

Fig. 4. Effect of initial pH value on the residual Ni(II) concentrations: (a) 50.00 mg l^{-1} free Ni(II) at stoichiometric dosages of precipitants; (b) NiCA containing 50.00 mg l^{-1} Ni(II) at 10% dose increase of BDP and DDTC.

3.2. Removal of complex nickel(II)

In practical industrial wastewater, nickel(II) frequently exists in a coordinated form. As is known, the traditional methods, such as adding alkaline, are powerless to treat complex nickel. Considering that H_3CA, a naturally occurring complexing agent, is often used in electroplating baths for various Ni alloys [21] and in modern microelectronic industries, NiCA was selected as a representation of nickel complexes and treated with BDP and DDTC in this section.

The experiment results showed the behaviors of BDP and NiCA reaction were slightly similar to that of BDP and free Ni(II) reaction. From Fig. 5b, after 5 min agitation following 1 min settling, the residual turbidity of the solution is 53 NTU. Although it is 6.5 times higher than the corresponding turbidity for the solution containing free Ni(II), it can still meet the effluent standard (70 NTU) of China EPAs regulation. Comparatively, the settling performance of DDTC as the precipitant of NiCA is not more favorable than that of BDP. It can be seen from Fig. 5b that the turbidity is 321 NTU after settling for 1 min and still remains 159 NTU even after 1 h. Furthermore, even adding aluminum sulfate as a coagulation agent, the turbidity only declined slightly.

As shown in Fig. 3b, at 1:1 stiochiometric dose of BDP/NiAC, the residual Ni^{2+} concentration in the filtrate was $2.38\ mg\ l^{-1}$, being 23.5-fold of the corresponding residual for the solution containing free nikel(II). The difference was simply contributed to the competition of CA with BDP in binding Ni(II). It was found that a slight excess of BDP dose was considerably beneficial to the precipitation reaction in the competition. When 10% dose increase in BDP, the residual concentration was decreased to $0.08\ mg\ l^{-1}$. With respect to DDTC, at stoichiometric dose of DDTC/NiAC, the residual concentration of nickel was $3.12\ mg\ l^{-1}$. When 10% dose increase of DDTC, the residual concentration was reduced to $0.30\ mg\ l^{-1}$. It was derived from the analysis of these results that, for both BDP and DDTC, a slight excess of stoichiometric dose would be needed in order to

treat NiAC-containing wastewaters to discharge limits, although the residual concentration of Ni(II) for BDP was slightly lower than that for DDTC.

The dependence of residual Ni(II) concentration on pH is depicted in Fig. 4b. As can be seen from the figure, the residual nickel concentrations after application of BDP were far below than that of DDTC when pH > 5, especially at basic conditions. Comparing Fig. 4a with b, it can be seen that BDP could be applied in neutral and basic solutions for either free Ni^{2+} or NiCA. In other words, the applicable pH range for BDP is independent on whether nickel ions are coordinated or not.

3.3. Simultaneous removal of Ni(II) and dye

Practical heavy metal wastewater may contain dyes and simultaneous removal of heavy metal ions and dyes have been investigated by scholars [22–25]. Majority of simultaneous removal methods is by adsorption. In our previous studies, the simultaneous removal of copper ions and Acid Red 73 by BDP was investigated [14]. In this section, our attention has been focused on the performances of BDP and DDTC as precipitants of the Ni(II)-dye integrated wastewaters. Because azo-dye is the largest-group of colorants used in a variety of industries ranging from textile to paper [26] and is of persistent and recalcitrant nature, an azo-dye, X-3B, was used as a test dye in the present study.

The dependence of the residual nickel(II) and X-3B concentrations on the molar ratio of precipitant/Ni(II) is presented in Fig. 6. It can be seen from this figure that both BDP and DDTC could quantitatively precipitate Ni^{2+} and the precipitation process was almost unaffected by the dye. Moreover, it was also observed that BDP still could partly remove the dye while DDTC did not possess this function. For example, the nickel and X-3B concentrations were decreased from 50.00 and $30.00\ mg\ l^{-1}$ to 0.87 and $19.52\ mg\ l^{-1}$, respectively, at the molar ratio of 1:1 (BDP/Ni) while the residual concentrations of nickel(II) and
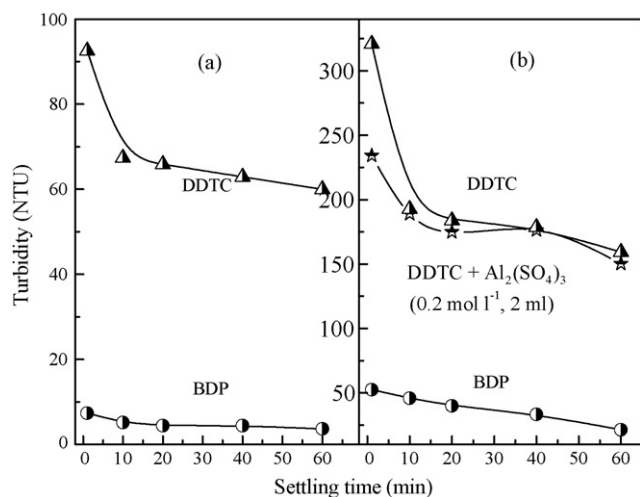

Fig. 5. Plot of turbidity vs. settling time after a 5 min agitation followed by addition of BDP or DDTC with an initial pH of 7.0: (a) $50.00\ mg\ l^{-1}$ free Ni(II); (b) NiCA containing $50.00\ mg\ l^{-1}$ Ni(II).
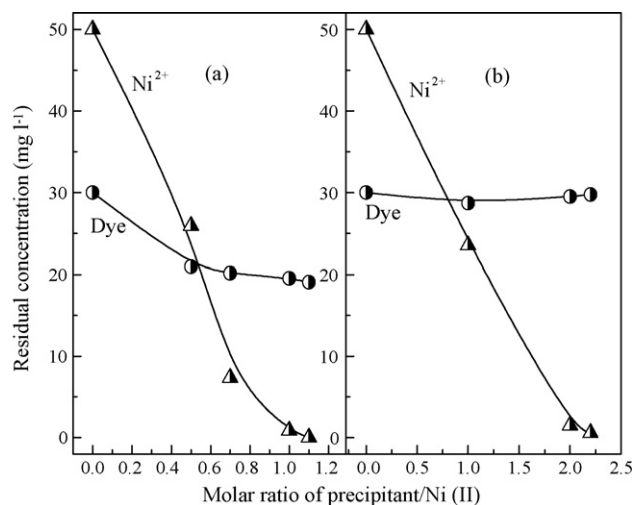
Fig. 6. Dependence of residual Ni^{2+} and X-3B concentration on the molar ratio of precipitant/Ni(II) in $50.00\ mg\ l^{-1}$ free Ni^{2+} and $30.00\ mg\ l^{-1}$ X-3B mixed solution with an initial pH of 7.0: (a) BDP; (b) DDTC.

Table 1
Langmuir and Freunlich isotherms constants for adsorption of X-3B by $[NiBDP]_n$ precipitates

Langmuir parameters				Freundlich parameters			
Q_0 (mg g^{-1})	b (l mg^{-1})	r^2	Δq (%)	a (mg g^{-1}) (l mg^{-1})^n	n	r^2	Δq (%)
243.72	0.0093	0.9914	24.74	8.90	1.84	0.9882	9.44

X-3B were 1.52 and 29.52 mg l^{-1}, respectively, at the molar ratio of 2:1 (DDTC/Ni).

The removal of the dye attracted us to further probe the removal mechanism because the decolorization of wastewater is also an environmental subject with a continuous interest in the past years. Fig. 7a presents UV–vis spectral change of the Ni(II)-dye solution with the molar ratio of BDP/Ni(II). As shown in the figure, no shift of absorption peak was observed although the absorption decreased rapidly with the increase of BDP. Moreover, additional experiments showed that single BDP or Ni^{2+} could not change the color of the dye solution. According to these facts, the removal of X-3B could be primarily attributed to its adsorption on $[NiBDP]_n$ precipitates, not to the chemical reaction between the $[NiBDP]_n$ or BDP and X-3B. In contrast, the X-3B concentration hardly decreased with the increase of DDTC as shown in Fig. 7b, further indicating that Ni(DDTC)$_2$ precipitates could not adsorb the dye.

In order to gain a quantitative understanding of the observed decolorization phenomena, isothermal adsorption experiments for X-3B on $[NiBDP]_n$ precipitates were conducted and the experimental data were analyzed using Langmuir and Freundlich models as given by the following equations, respectively:

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

$$q_e = a C_e^{1/n} \qquad (3)$$

where q_m is the maximum amount of adsorption (mg g^{-1}), b the adsorption equilibrium constant (l mg^{-1}), C_e the equilibrium concentration of X-3B in the solution (mg l^{-1}), a the constant representing the adsorption capacity (mg g^{-1})(l mg^{-1})^n, and n is the constant depicting the adsorption intensity.

The validity of isotherm models is tested by comparing the experimental and calculated data (Fig. 8) and the isotherm parameters that minimizes the sum of the errors square using Microcal Origin 7.0 are listed in Table 1. From Table 1, the maximum adsorption amounts of X-3B on $[NiBDP]_n$ precipitates was 243.72 mg g^{-1}. The Freundlich adsorption intensity, n, is between 1 and 10, indicating that the adsorption was a favorable process [27]. Both the Langmuir and Freundlich equation can represent the adsorption process well for the R^2 values were both higher than 0.988, indicating a good mathematical fitness. To quantitatively compare the fitness of the two models, a normalized standard deviation Δq (%) was calculated by the following formula [28].

$$\Delta q\,(\%) = 100 \sqrt{\frac{\sum_{i=1}^{N}[((q_{exp} - q_{cal})/q_{exp})^2]}{N-1}} \qquad (4)$$

where N is the number of data points, and q_{exp} and q_{cal} are the experimental and calculated q_e values, respectively. The calculation results in Table 1 show the Δq (%) value obtained from the Freundlich is smaller than that from the Langmuir equation. The fact suggests the Freundlich equation is more suitable than the Langmuir for the description of the adsorption equilibrium.

Based on the above facts and analysis, expectedly, BDP can be employed to simultaneous removal of Ni^{2+} and dye from the integrated wastewater.
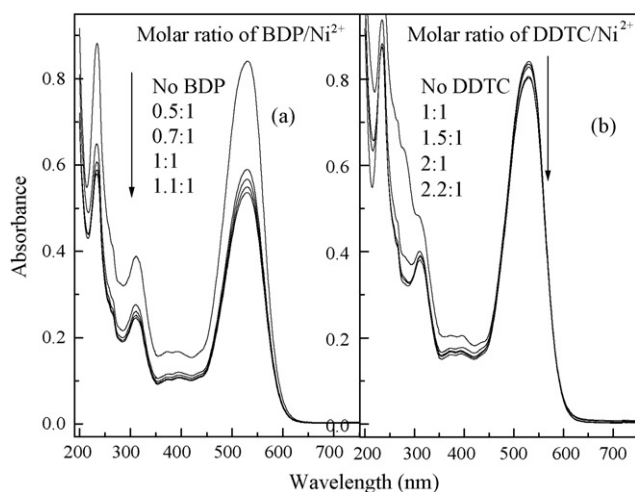

Fig. 7. Change of UV–vis spectra of X-3B with the molar ratio of precipitant/Ni(II) in the 50.00 mg l^{-1} Ni^{2+} and 30.00 mg l^{-1} X-3B mixed solution with an initial pH of 7.0: (a) BDP; (b) DDTC.
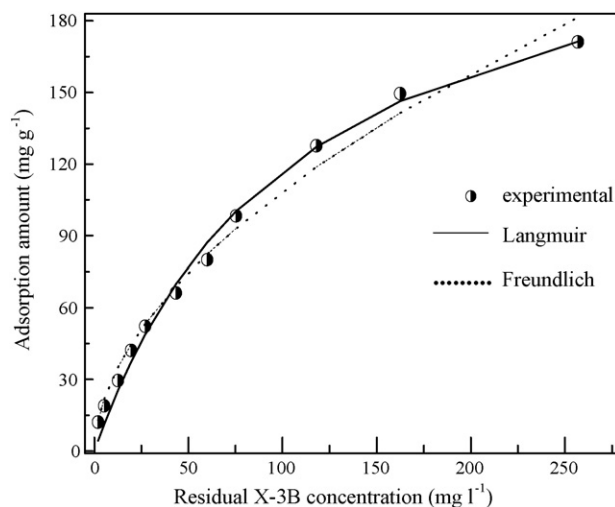

Fig. 8. Adsorptions isotherm of X-3B on $[NiBDP]_n$ precipitates (dot: experimental point, solid line: fitted line with Langmuir mode, dot line: fitted with Freundlich mode).

4. Conclusions

As the heavy metal Ni(II) precipitant, BDP displayed many advantages over DDTC. Two of these advantages were more obvious.

(1) BDP coordination polymerization precipitates possessed a more rapid settling speed than DDTC precipitates.
(2) BDP could not only efficiently precipitate Ni^{2+} but also partly remove X-3B from Ni^{2+}-dye integrated wastewater through the adsorption function of the precipitate $[NiBDP]_n$.

Acknowledgements

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