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Preparation and Analytical Study of New Chelating Resin Containing Tetracycline Drug

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Abstract

A new chelating resin was prepared by mixing tetracycline drug and trimethylolphenol. It was polymerized by heating to 90 °C then it was post cured to 100 °C after that it was grinded. The chelating behavior was examined against Co(II), Ni(II) and Cr(III) using patch method in different conditions like treatment time and pH at room temperature. The resin shows a good loading capacity toward Co(II) (time = 24 hrs and pH = 4) = 12.24 mg ion/ g resin, Cr(III) (time = 24 and pH = 4) = 11.21 mg ion/ g resin, and Ni(II) (time = 4 hrs and pH = 2) = 9.3 mg ion/ g resin.

Keywords: Tetracycline, Loading capacity, Chelating resin.

1. Introduction

Chelating resins have been widely used for separating and treating industrial wastewater which contains heavy metal ions[1-3]. There are a large number of hydrophilic groups such as –CH₂OCH₂- and –CH₂OH in the structure of phenol-formaldehyde, which confer excellent hydrophilic and swelling properties upon the resin in water and other polar solvents.[4] Therefore, phenol-formaldehyde resin is more suitable than those hydrophilic polymers such as crosslinked polystyrene and crosslinked polyacrylate for preparing ion-exchangers

or chelating agents used in polar solvents[5].

Metal ion uptake properties of polystyrene-supported chelating polymer resins functionalized with (i) glycine, (ii) hydroxy benzoic acid, (iii) Schiff base and (iv) diethanol amine have been investigated by A. R. Reddy and K. H. Reddy[6]. The effects of pH, time and initial concentration on the uptake of metal ions have been studied. They found that the uptake of metal ion depends on pH. The resins are more selective at pH 10 for Pb(II) and Hg(II),

whereas at pH 6 were found to be Cd(II) and Cr(VI) selective.

Shah and coworkers[7] synthesized the chelating resin based on phthalic acid-formaldehyde-resorcinol (PFR) and characterized by FTIR and elemental analysis. The resin had been studied as chelating sorbent for several metal ions [Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II)]. The ion exchange capacity order is Ni(II) > Zn(II) > Cu(II) > Cd(II) > Pb(II). The ion exchange capacity for Cu(II) was 0.9736 mmol/g of dry resin.

Roy and coworkers[8] prepared a new chelating polymer sorbent from the copolymerization of styrene and maleic anhydride in the presence of divinyl benzene as the crosslinking agent, followed by hydrolysis. This polymeric resin, bearing O donor groups, had the advantage of being stable in the basic and saline media, unlike its linear analogue. This newly developed chelating matrix has a high resin capacity for metal ions such as Cr, Fe, Ni, Cu, and Pb. Various physicochemical parameters, such as the pH, volume, and flow rate, and the interference effect on metal uptake were studied. The sorption capacities of the crosslinked resin for Cr(III), Fe(III), Ni(II), Cu(II), and Pb(II) were (10.2, 14.3, 14.2, 15.4, and 8.8) mg/g, respectively.

2. Experimental part

The chelating resin was prepared by mixing the Methylol (2,4,6-trimethoxyphenol) with tetracycline then it was polymerized by heating to 90 °C then it was post cured to 100 °C after that it was grinded. The polymerization steps and the resulting polymer containing encapsulated tetracycline are shown in Scheme 1 and 2, respectively. The chelating behavior was examined against Co(II), Ni(II) and Cr(III) using patch method by shaking 0.1g of resin

Samal and coworkers[9] synthesized two chelating resins with multiple functional groups. The chelating resins were synthesized by condensing a phenolic Schiff base derived from 4,4-diaminodiphenylmethane and *o*-hydroxyacetophenone with formaldehyde or furfuraldehyde. The resins readily absorbed transition metal ions, such as Cu²⁺ and Ni²⁺, from dilute aqueous solutions. The extent of metal-ions loading into the resins were studied in competitive and noncompetitive conditions, varying the time of contact, metal ion concentrations, and pH of the reaction medium in a suitable buffer medium. The furfuraldehyde-condensed resin was more effective in removing metal ions than the formaldehyde-condensed resins. The resins were selective for Cu²⁺, resulting in separation of Cu²⁺ and Ni²⁺ from the mixture at pH 5.89.

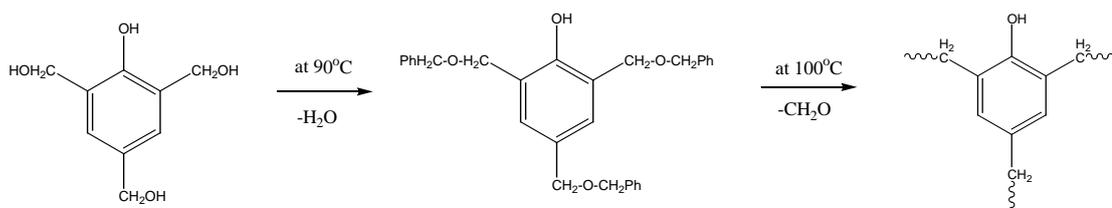
The present work involves preparation of a new chelating resin from the reaction between tetracycline drug and trimethylolphenol, then study the chelating behavior of this resin through calculating the loading capacity against Co(II), Ni(II) and Cr(III) in different conditions like treatment time and pH at room temperature.

with 0.1g/l metal solution in different conditions like treatment time (0.5, 1, 2, 3, 4 and 24) hrs and pH at room temperature. The solution was filtered and the remaining concentration of metal in the filtrate was measured by taking the absorption and using the standard calibration curve for each element. The loading capacity for each treatment was measured by calculating the differences between the primary

concentration and the concentration of the filtrate.[10]

Stock solutions of Co(II), Cr(III) and Ni(II) were prepared from high purity grade as nitrate salts using demineralized water in pH of 2, 4, and 6 using nitric acid. The loading capacity of the resin toward Co(II), Cr(III) and Ni(II) was determined using

Phenix Range UV-Visible spectrophotometer. The maximum absorption wavelengths (λ_{\max}) were identified for Co(II) ($\lambda_{\max}=580\text{nm}$), Cr(III) and Ni(II) ($\lambda_{\max}=570\text{nm}$), then all absorption measurements were carried out in the same wavelength for each element.



Scheme 1

Scheme 2

The standard calibration curve for each element was measured by taking the absorption for series concentrations (5, 10, 20, 40, 60, 80 and 100) mg/L of standard

solution for each element. Table 1 and Figure 1 illustrate the standard calibration curve for Co(II).

Table 1 The calibration curve data for Co(II)

Concentration (mg/L)	Absorbance
0	0
5	0.002
10	0.004
20	0.011
40	0.029
60	0.046
80	0.061
100	0.079

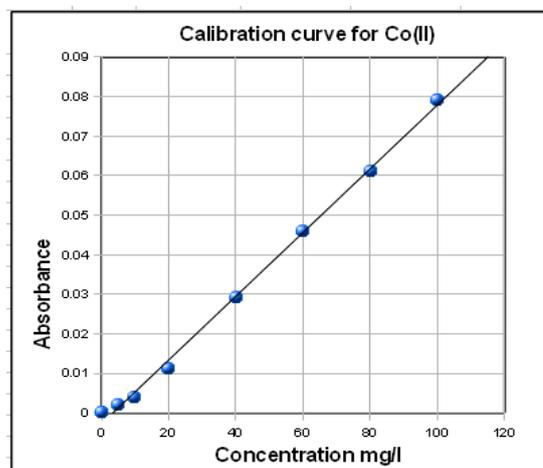


Figure 1 The calibration curve for Co(II)

3. Results and discussion

In this study two main factors that may affect on the loading capacity which are treatment time and pH change. For each one of these conditions, the effect of changing on the loading capacity was made by

making all other affecting factors constant, such as temperature and initial concentration on the uptake of metal ions. In this study, three metal ions were studied Ni²⁺, Cr³⁺ and Co²⁺.

3.1 Chelating behavior of the resin toward Ni²⁺ ions:

a- Effect of treatment time on the loading capacity

Table 2 and Figure 2 show the effect of treatment time on the loading capacity. We see that the increasing of treatment time will lead to increase the loading capacity until treatment time of 4 hrs, after that there is no effect of increasing treatment time on the loading capacity for all studied pH. Therefore, the best treatment time is 4 hrs

which can be explained as the treatment time of the resin with Ni²⁺ ions the ability of resin to make more chelating bonds with Ni²⁺ until 4 hrs of treatment, after this time the resin will no longer be able to make chelating bonds with Ni²⁺, so the loading capacity will remain constant as the treatment time increased.

Table 2 The effect of treatment time on the loading capacity for Ni²⁺ ions

Loading capacity (mg ion/ 100 mg resin)	time hour	pH
1.02	0.5	2
4.23	1	2
7.1	2	2
8.1	3	2
9.3	4	2
9.3	24	2
0.89	0.5	4
3.55	1	4
6.4	2	4
7.75	3	4
9.1	4	4
9.1	24	4
0.76	0.5	6
3.55	1	6
6.4	2	6
7.76	3	6
8.88	4	6
8.88	24	6

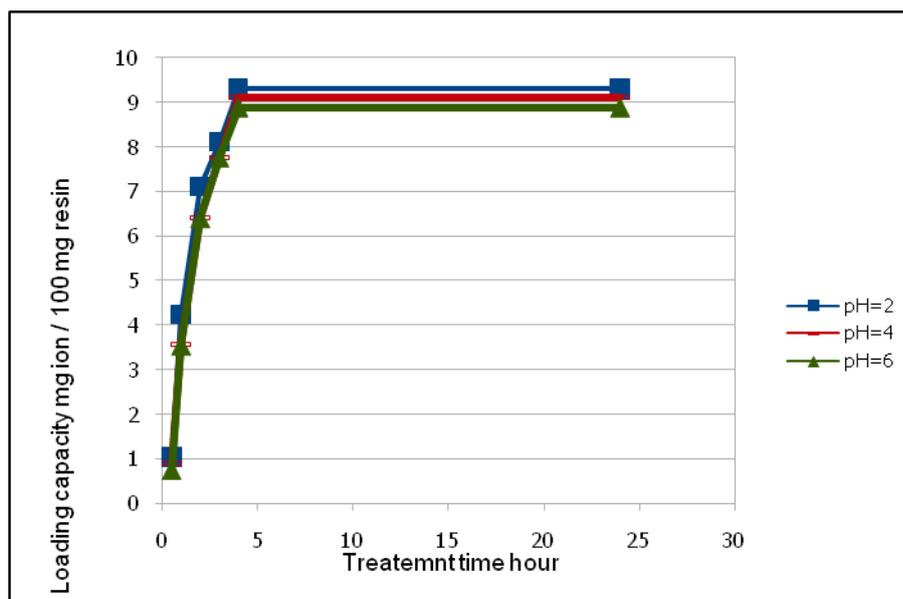


Figure 2 The effect of the treatment time on the loading capacity for Ni²⁺ ion at different pH

b- Effect of pH on the loading capacity

The loading capacity for Ni²⁺ ion was studied in three pH, 2,4 and 6. The maximum loading capacity in all studied the time was in pH = 2, as shown in Table 3 and Figure 3. In this pH, which is strongly acidic medium, the chelating atoms in the

resin are more powerful to withdraw the Ni²⁺ ions from the solution. This might be explained that the chelating site steric shape or steric configuration is in the best share to make coordination bonds with Ni²⁺ ions.

Table 3 The effect of pH on the loading capacity for Ni²⁺ ions

Loading Capacity (mg ion/ 100 mg resin)	pH	Time (hr)
1.02	2	0.5
0.89	4	0.5
0.76	6	0.5
4.23	2	1
3.55	4	1
3.55	6	1
7.1	2	2
6.4	4	2
6.4	6	2
8.1	2	3
7.75	4	3
7.76	6	3
9.3	2	4
9.1	4	4
8.88	6	4
9.3	2	24
9.1	4	24
8.88	6	24

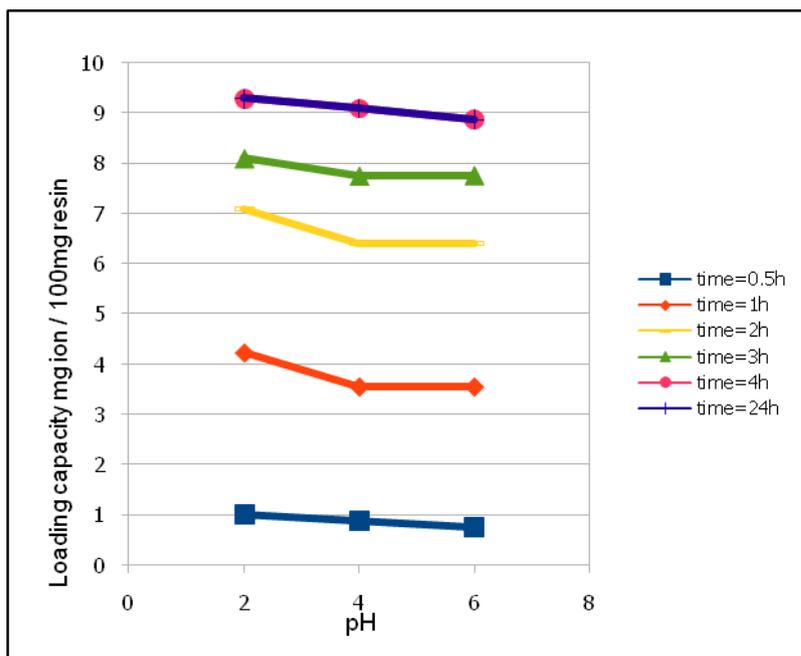


Figure 3 The effect of pH on the loading capacity for Ni²⁺ ion

3.2 Chelating behavior of the resin toward Cr³⁺ ions:

a- Effect of treatment time on the loading capacity

Table 4 and Figure 4 show the relationship between the loading capacity and the treatment time. As the treatment time increases the loading capacity will increase for all studied pHs, this might be

explained that the resin is able to make more coordination bonds with Cr³⁺ as the treatment time increases and withdrawing more Cr³⁺ ions from solution.

Table 4 The effect of treatment time on the loading capacity for Cr³⁺ ions

Loading capacity (mg ion/ 100 mg resin)	time hour	pH
3.43	0.5	2
3.98	1	2
6.18	2	2
6.73	3	2
7.82	4	2
7.94	24	2
3.71	0.5	4
3.98	1	4
6.43	2	4
6.93	3	4
7.39	4	4
7.5	24	4
5.53	0.5	6
7.28	1	6
8.22	2	6
9.45	3	6
10.86	4	6
11.21	24	6

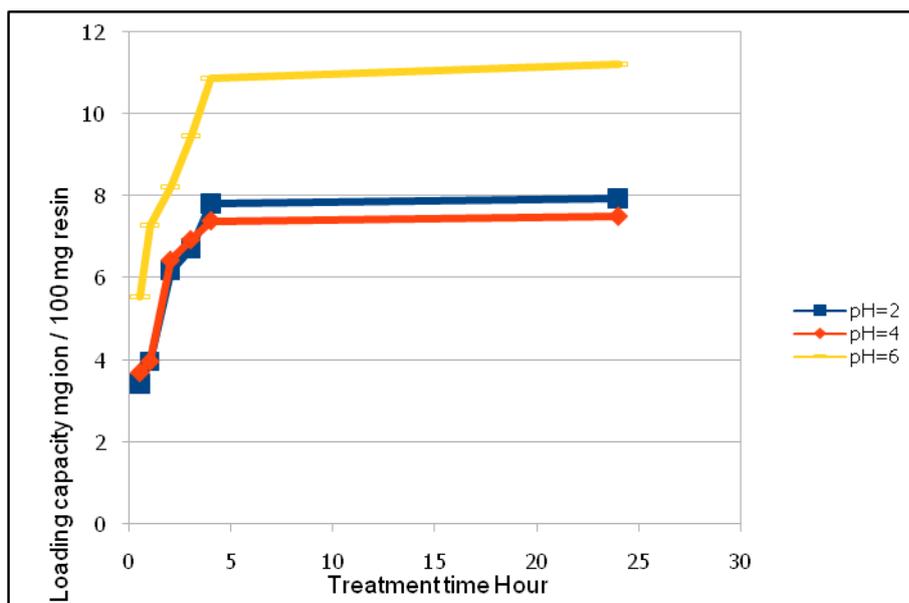


Figure 4 The effect of the treatment time on the loading capacity for Cr^{3+} ion at different pH

b- Effect of pH on the loading capacity

Table 5 and Figure 5 show the effect of pH on the loading capacity the resin toward Cr^{3+} ions. The figure shows that the pH value has significant effect on the loading capacity of the resin, the maximum loading capacity is in pH=6 for all studied treatment time. There is large difference in the loading capacity between pH=6 and pH=2,4 and the

loading capacity increases as the pH increased. This might be interrupted that at pH=6 which is near a neutral so many atoms in the chelate sites have a good ability to make coordination bonds with Cr^{3+} , so that will lead to increase the loading capacity.

Table 5 The effect of pH on the loading capacity for Cr^{3+} ions

Loading Capacity (mg ion/ 100 mg resin)	pH	Time (hr)
3.43	2	0.5
3.71	4	0.5
5.53	6	0.5
3.98	2	1
3.98	4	1
7.28	6	1
6.18	2	2
6.43	4	2
8.22	6	2
6.73	2	3
6.93	4	3
9.45	6	3
7.82	2	4
7.39	4	4
10.86	6	4
7.94	2	24
7.5	4	24
11.21	6	24

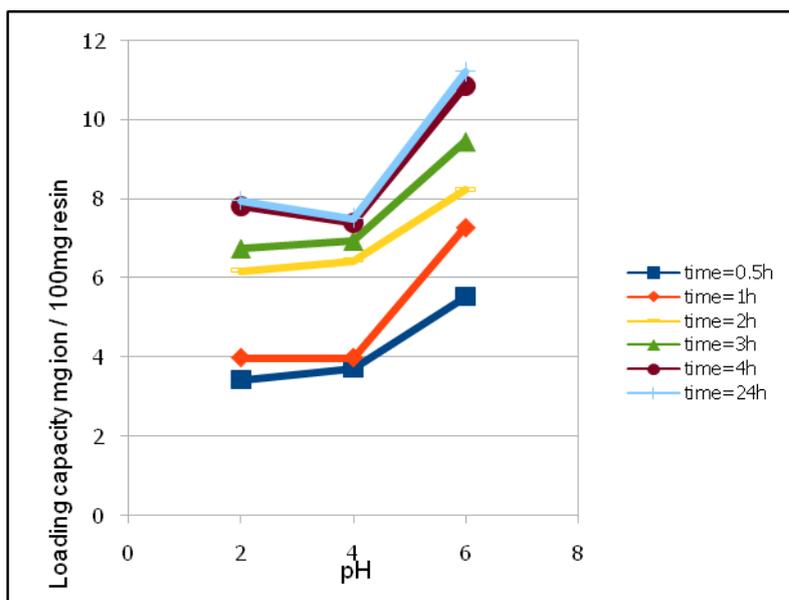


Figure 5 The effect of pH on the loading capacity for Cr³⁺ ion

3.3 Chelating behavior of the resin toward Co²⁺ ions:

a- Effect of treatment time on the loading capacity

Table 6 and Figure 6 show the relationship between the loading capacity and the treatment time. There is proportional relationship between the loading capacity toward Co²⁺ and the treatment time, as the treatment time

increases the loading capacity will increase at the three pH values, this might be explained that the resin is able to make more coordination bonds with Co²⁺ as the treatment time increases and withdrawing more Co²⁺ ions from solution.

Table 6 The effect of treatment time on the loading capacity for Co²⁺ ions

Loading capacity (mg ion/ 100 mg resin)	time hour	pH
3.79	0.5	2
4.64	1	2
5.5	2	2
6.96	3	2
8.42	4	2
8.42	24	2
5.26	0.5	4
6.23	1	4
6.72	2	4
8.42	3	4
10.13	4	4
12.56	24	4
5.01	0.5	6
6.11	1	6
6.47	2	6
7.69	3	6
10.13	4	6
12.24	24	6

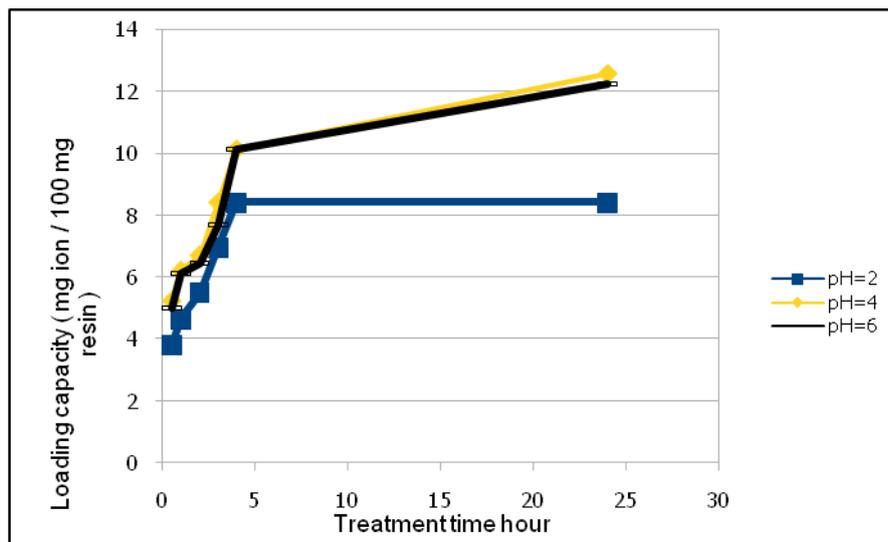


Figure 6 The effect of the treatment time on the loading capacity for Co^{2+} ion at different pH

b- Effect of pH on the loading capacity

Table 7 and Figure 7 illustrate the relationship between the pH and the loading capacity. The maximum loading capacity in pH=4 in all studied treatment times, except at treatment time of 4 hrs the loading capacity at pH=4 is equal to the loading capacity at pH=6. The maximum loading

capacity at pH of 4 may be attributed to that at this pH the chelating site steric configuration is in the best shape to make coordination bonds with Co^{2+} ions, so more coordination bonds will lead to increase the loading capacity.

Table 7 The effect of pH on the loading capacity for Co^{2+} ions

Loading Capacity (mg ion/ 100 mg resin)	pH	Time (hr)
3.79	2	0.5
5.26	4	0.5
5.01	6	0.5
4.64	2	1
6.23	4	1
6.11	6	1
5.5	2	2
6.72	4	2
6.47	6	2
6.96	2	3
8.42	4	3
7.69	6	3
8.42	2	4
10.13	4	4
10.13	6	4
8.42	2	24
12.56	4	24
12.24	6	24

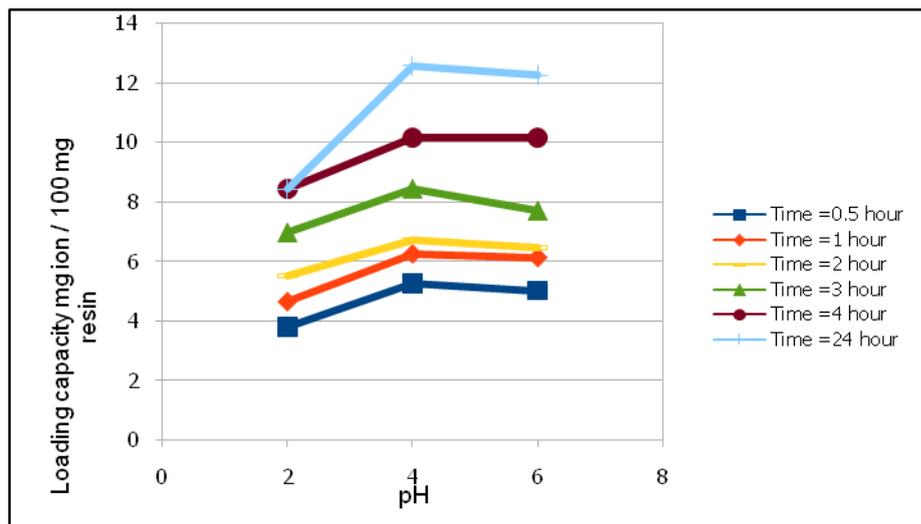


Figure 7 The effect of pH on the loading capacity for Co²⁺ ion

4. Conclusions

The presence of heavy metal ions, viz. Co(II), Cr(III) and Ni(II), in aquatic systems pose heavy risks to human health. Therefore, the removal of such metal ions from water bodies may be considered an interesting and important research activity.

Chelating resins are stable, and can be used for the removal of metal ions at room temperature. Their metal uptake efficiency clearly depends on pH and reaches a plateau at pH 4 for Co(II) and Cr(III), and pH 2 for Ni(II).

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