



## Recovery of nickel from aqueous samples with water-soluble carboxyl methyl cellulose–acetone system

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### ABSTRACT

A simple and efficient method, which involves carboxyl methyl cellulose (CMC) and acetone, was developed for recovery of trace nickel from aqueous solutions. This method was based on the fact that Ni<sup>2+</sup> could react with CMC and form water-soluble complexes, which would solidify in excess acetone. After centrifugation, the solid mass consisting of the nickel complex and free CMC was easily dissolved with water and the nickel was determined by flame atomic absorption spectrometry (FAAS). Several factors influencing the recovery of nickel were thoroughly investigated and the optimized conditions were as follows: 5.00 mL water sample, 0.50 mL 0.5% CMC, 1.00 mL of 3.0 mg mL<sup>-1</sup> KNO<sub>3</sub> and 20 mL acetone. Under the optimized conditions, the loading capacity of CMC for nickel was 20.6 mg Ni/g polymer. The linear range was 0.025–3.0 μg mL<sup>-1</sup>, the limit of detection was 0.019 μg mL<sup>-1</sup> and the pre-concentration factor was 4. Ni(II) can be well recovered in this CMC–acetone system from binary ions mixtures containing Zn(II), Ba(II), Ca(II), Mo(VI), Co(II), Cd(II), Mg(II), Mn(II) and Cr(III). The developed method had been applied to the recovery of trace nickel in water samples with satisfactory results. A possible mechanism for the nickel precipitate was proposed. The efficient, convenient and affordable method provides an alternative method for the recovery of nickel from environmental waters.

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### 1. Introduction

Nickel is an important element due to its high strength and resistance to corrosion in many media. It is used in nickel plating and also in the manufacture of alloys along with iron, copper, aluminum, chromium, zinc and molybdenum. As a result of its wide industrial applications, nickel has become an important contaminant in aquatic environment since it is a toxic heavy metal and some of its compounds are carcinogenic. Moreover, these toxic nickel compounds cannot be easily degraded and destroyed if they were released into environments. Therefore, there is a growing need for developing simple methods capable of separating and recovering trace nickel from environmental waters.

The removal and recovery of heavy metal ions from aqueous solutions has been traditionally carried out by chemical precipitation, ion exchange, adsorption, etc. Nowadays, the ultrafiltration method for trace metals removal from waters by the addition of water-soluble polymers into the aqueous solutions

has become a significant research area. This method is based on the principles that the polymers with a large molecular weight can bind heavy metal ions to form macromolecular complexes. Their metal complexes can be retained and concentrated by ultrafiltration membrane, whereas the unbound metal ions pass through the membrane. Up to now, many polymers such as polyethyleneimine [1–3], poly(acrylic acid) [4–6], poly(vinyl alcohol) [7,8], poly(diallyl dimethylammonium chloride) [9], polyethyleneimine N-methylhydroxamic acid [10], poly(sodium 4-styrenesulfonate), poly(allylamine) [11], poly[acrylamide-co-1-(2-hydroxyethyl)aziridine] [12], N-benzoylthiourea modified polyamidoamine dendrimers [13], partially ethoxylated polyethyleneimine [14], poly(dimethylamine-co-epichlorohydrin-co-ethylene-diamine) [15] and diethylaminoethyl cellulose [16], carboxyl methyl cellulose [17], chitosan and pectin [18] were used for metals removal from wastewaters. Recently, a simple and effective technique for separation and pre-concentration of metal ions has been proposed as the same requires the use of water-soluble polymer in ultrafiltration process. In this technique, the water-soluble polymer added to the sample solutions forms complexes with metal ions and the reaction products, the metal–polymer complexes, precipitate immediately in excess acetone. Therefore, the metal ions convert into the solid phase and are separated from moderate amounts of aqueous matrixes. Then, the precipitate

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**Table 1**  
Flame atomic absorption spectrophotometer conditions for the determination of nickel.

Lamp current	Wavelength	Slit	Flame	Oxidant gas pressure	Fuel gas flow rate
12 mA	232.0 nm	0.2 nm	Air–acetylene	160 kPa	2.2 L min <sup>-1</sup>

including the metal–polymer complexes and the free water-soluble polymer was separated and dissolved in water. Finally, the metal ions were determined by suitable detectors. The water-soluble polymer–acetone system had been applied successfully in some research works due to its rapid phase separation and high enrichment capacity. For example, Bakırcıoğlu et al. [19] described the use of polyacrylic acid for the determination of Cu<sup>2+</sup>, Cd<sup>2+</sup> and Zn<sup>2+</sup>. Özcan et al. [20] investigated the use of polyacrylamide containing R-(+)-cystein end groups for the determination of Cu<sup>2+</sup>, Pb<sup>2+</sup> and Cr<sup>3+</sup>. Other water-soluble polymers such as poly(vinyl pyrrolidone) for the determination of lead, copper, manganese, nickel and cobalt [21,22] and polyethylenimine for the determination of copper and manganese [23] had been investigated in detail.

Sodium carboxyl methyl cellulose (CMC) is known to be a derivative of cellulose that is colorless, odorless, non-toxic and water soluble. It also possesses good complexation ability for some metal ions, such as Cu<sup>2+</sup>, Cd<sup>2+</sup>, Co<sup>2+</sup>, Zn<sup>2+</sup>, Ni<sup>2+</sup> and Pb<sup>2+</sup> [24], and is chosen as the macromolecular complexing agent for the selective removal and recovery of copper from water in complexation–ultrafiltration process [17]. Up to now, no paper has been found about the use of the CMC–acetone system for the separation and pre-concentration of nickel.

The main objective of this paper is to study the applicability of the CMC–acetone system for the removal and recovery of nickel from aqueous solutions. The factors affecting the recovery of nickel were optimized. This technique was also evaluated by recovering nickel from real water samples. The possible mechanism of the proposed technique was discussed according to electrical conductivity and ultraviolet–visible spectra experiments.

## 2. Experimental

### 2.1. Apparatus and reagents

A Z-5000 atomic absorption spectrometer (Hitachi Ltd., Tokyo, Japan) was used for absorption measurements, the instrumental parameters for the determination of nickel were adjusted according to the manufacturer's recommendations, as shown in Table 1. All electric conductivity measurements were performed with a Model DDS-307 electric conductivity meter fitted with a model DJS-1 electric conductivity electrode (Shanghai Rex Instrument Factory, China). A Shanghai pHs-2 pH meter fitted with a combination glass electrode was employed for pH measurements. A Perkin-Elmer Lambda 17 UV/Vis spectrometer was used to scan UV spectra. A model TDL-40B centrifuge instrument (Shanghai Anting Scientific Instrument Factory, China) was used to speed up the precipitation.

All reagents were of analytical grade. A standard stocks solution of Ni<sup>2+</sup> (1.0 mg mL<sup>-1</sup>) was prepared by dissolving 0.4784 g of nickel sulfate heptahydrate (Shanghai Reagents Plant, Shanghai, China) in distilled water containing small amount of 1:1 H<sub>2</sub>SO<sub>4</sub> and diluted to the mark in a 100 mL volumetric flask. All working solutions of Ni<sup>2+</sup> were prepared daily by serial dilution of the stock solution. 0.5% (w/v) CMC was prepared by dissolving appropriate amounts of CMC (Shantou Xilong Chemical Factory, Guangdong, China) in distilled water. The pH values of solutions were adjusted by using diluted HCl or NaOH and measured with the pH meter. Solutions of alkali metal salts including KNO<sub>3</sub>, KCl, NaCl and KSCN were used to study the salting-out effect. Distilled water was obtained by distillation from deionized water and used whenever required.

### 2.2. General procedure

An aliquot of 5.00 mL aqueous solutions containing the nickel was placed in a 50 mL centrifuge tube, 0.50 mL 0.5% CMC was added to the solution. Then 1.00 mL of 3.0 mg mL<sup>-1</sup> KNO<sub>3</sub> solution and 20 mL acetone were added to the above solution, respectively. The Ni–CMC complex and free CMC molecules were precipitated immediately. In order to speed up the precipitation, the tube was centrifuged at 1800 rpm for 3 min. The supernatant was separated by decantation. The precipitate was dissolved in small amount of distilled water and then diluted to 2.50 mL for FAAS measurements.

### 2.3. Loading capacity of the CMC

The loading capacity of the polymer for the nickel was determined by using excessive nickel ions and following the general procedure. After reaching equilibrium, the equilibrium concentration of nickel in the supernatant was determined by the atomic absorption spectrometer. Then the loading capacity was calculated using the following formula:

$$q_e = \frac{M_0 - C_e V}{m} \quad (1)$$

where  $q_e$  is the equilibrium loading capacity in mg g<sup>-1</sup>;  $M_0$  is the mass of nickel ions added in mg;  $C_e$  are the equilibrium concentration of nickel ions in supernatant in mg mL<sup>-1</sup>;  $V$  is the volume of the supernatant in mL and  $m$  is the mass of the polymer added in g.

### 2.4. Measurement of electrical conductivity

A series of 5.00 mL solutions with different concentration of nickel ions were added into 50 mL centrifuge tubes. Other series of 5.00 mL solutions were prepared with the same concentration of nickel in the corresponding centrifuge tubes, then 0.50 mL 0.5% CMC was added into the solution for each centrifuge tube. The change of the electrical conductivity of above solutions was measured.

## 3. Results and discussion

As it is well known, the recovery process of metal ions can be affected by several experimental parameters, including sample pH, acetone amount, salting-out effect and complex reaction time. The study and optimization of the above-mentioned variables were performed by modifying one at a time while keeping the remaining constant. A 5.00 mL aqueous solution containing 1.0 μg mL<sup>-1</sup> of Ni<sup>2+</sup> was used to perform the experiments.

### 3.1. Effect of sample pH on the recovery of nickel

CMC is anionically charged polysaccharides. The structure of its basic unit is shown in Fig. 1. In near neutral to basic solution, the carboxymethyl would dissociate and then complex with nickel ions. Hence, the pH value of the aqueous solutions is a critical parameter to achieve high recoveries for target metal ions in water-soluble polymer–acetone system. The effect of aqueous solution pH on recovery of Ni<sup>2+</sup> in the range of 1.0–9.0 was evaluated. The results are presented in Fig. 2. As can be seen in Fig. 2, the recovery of nickel was firstly increased with pH value increase until the recovery reaches its maximum at pH 5.0 and then maintained a flat profile

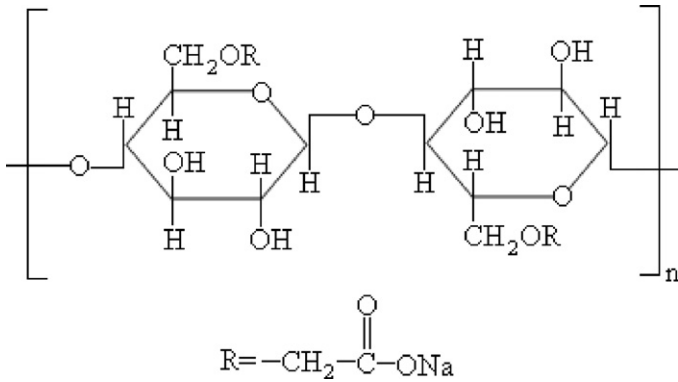


Fig. 1. Molecular structure of CMC.

when the pH was changed from 5.0 to 9.0. The observation may be attributed to the relationship between the  $pK_a$  of CMC and the pH of the aqueous solution. It is well known that the CMC has a  $pK_a$  smaller than 5.0 [25]. Therefore, at a pH below 5.0, CMC could be an acid compound. In other words, a great amount of the  $H_3O^+$  occupies the position to prevent the target metal ions to form complexes with CMC. The metal bonding is expected to be low and the metal decomplexation can occur. With the increase of pH, more and more carboxymethyl dissociate gradually and complex with nickel ions. Thus, the pH of the aqueous solution should be higher than 5.0 for CMC to completely form complexes with target metal ions.

### 3.2. Effect of acetone amount on the recovery of nickel

The effect of acetone amount on recovery of nickel was examined in the range of 5–35 mL, the relations between the volume of acetone added and the recovery of nickel can be seen in Fig. 3. The recovery of nickel increases significantly with the increase of the volume of acetone and reaches its maximum when the volume of acetone is 20 mL. After 20 mL, the recovery of nickel was basically constant and no dramatic increase was observed with the additional volume of acetone. This may be attributed to the fact that 20 mL of acetone was enough to make the formed bulky Ni–CMC complex to be completely precipitated under the experimental conditions. Therefore, 20 mL was chosen as the optimum acetone volume.

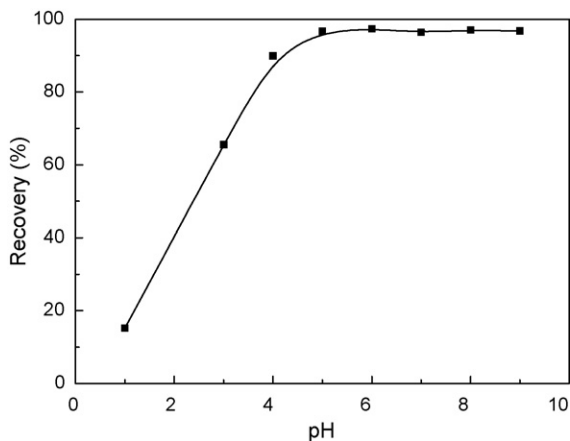


Fig. 2. Effect of pH value of solutions on nickel recovery. Conditions:  $5.0 \mu\text{g Ni}$ ,  $0.50 \text{ mL } 0.5\% \text{ CMC}$ ,  $1.00 \text{ mL of } 3.0 \text{ mg mL}^{-1} \text{ KNO}_3$ ,  $20 \text{ mL acetone}$ .

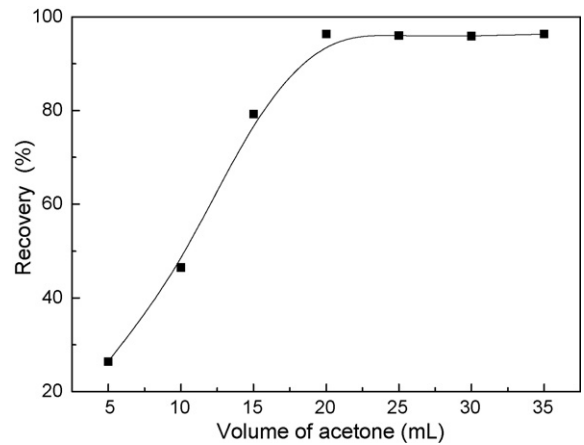


Fig. 3. Effect of volume of acetone on nickel recovery. Conditions:  $5.0 \mu\text{g Ni}$ ,  $0.50 \text{ mL } 0.5\% \text{ CMC}$ ,  $1.00 \text{ mL of } 3.0 \text{ mg mL}^{-1} \text{ KNO}_3$ .

### 3.3. Effect of salting-out agent on the recovery of nickel

The salting-out effect has been frequently used to improve extraction recovery. For this purpose, the effects of salting-out agents on the recovery of nickel were performed by adding different volumes of various salts including  $\text{KNO}_3$ ,  $\text{KCl}$ ,  $\text{NaCl}$  and  $\text{KSCN}$  to the aqueous solution. As demonstrated in Fig. 4, the recovery of nickel increased significantly with the addition of various salt solutions. One possible reason contributing to these findings is the decreased solubility of the Ni–CMC complex in aqueous sample when various salts were added to the aqueous sample. With the further increase of volume of salt solutions, the recovery of nickel begins to decrease. This may be attributed to the salting-in effect at higher concentration of the salts. Of these salts, the higher recovery of nickel was obtained with the addition of  $\text{KNO}_3$ . Hence,  $1.00 \text{ mL of } 3.0 \text{ mg mL}^{-1} \text{ KNO}_3$  was used for further experiments.

### 3.4. Effect of complex reaction time

The effect of complex reaction time on the recovery of nickel was discussed. It was found that the recovery of nickel was no less than 96% when the reaction time was in the range of 1–25 min. This means that nickel is quantitatively recovered with high precision and the kinetics of the complex reaction is fast. The similar results were reported in other water-soluble

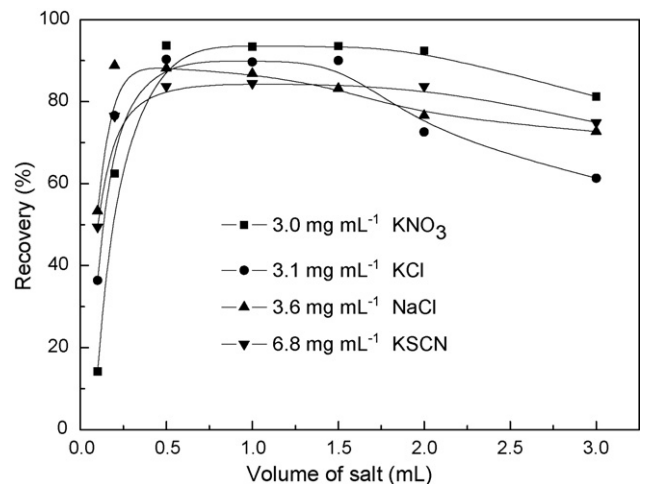


Fig. 4. Effect of salting-out agent on the recovery of nickel. Conditions:  $5.0 \mu\text{g Ni}$ ,  $0.50 \text{ mL } 0.5\% \text{ CMC}$ ,  $20 \text{ mL acetone}$ .

**Table 2**  
Loading capacity of some water-insoluble materials.

Adsorbents	Adsorbate	Loading capacity (mg g <sup>-1</sup> )	References
Natural iron oxide-coated sand	Cu <sup>2+</sup> , Ni <sup>2+</sup>	2.04, 1	[26]
Clinoptilolite	Ni <sup>2+</sup>	3.28	[27]
Carbon nanotubes (CNTs) and oxidized CNTs	Ni <sup>2+</sup>	18.1, 49.3	[28]
Peat moss	Cu <sup>2+</sup> , Ni <sup>2+</sup>	17.6, 14.5	[29]
Exhausted olive cake ash	Ni <sup>2+</sup> , Cd <sup>2+</sup>	8.38, 7.32	[30]
Na-mordenite	Ni <sup>2+</sup>	5.32	[31]
Activated carbon	Ni <sup>2+</sup>	17.2	[32]
Waste pomace of olive oil factory	Ni <sup>2+</sup>	14.8	[33]

polymer–acetone systems for the pre-concentration and separation of metals [19–23].

### 3.5. Loading capacity of CMC

To determine the loading capacity of CMC, experiments were performed at various initial concentration of Ni<sup>2+</sup> solution ranging from 75.0 to 120.0 μg (viz., 75.0, 100.0 and 120.0 μg). For each initial Ni<sup>2+</sup> concentration, the experiment was repeated for three times. The calculated loading capacity of CMC was 20.6 mg Ni/g polymer, which was the average by taking three initial Ni<sup>2+</sup> concentrations. This is considerably high capacity with respect to many water-insoluble materials (see Table 2) [26–33] and the loading capacity of the CMC also has the same magnitude order with respect to many water-soluble polymers. For example, the loading capacity of polyacrylamide containing R-(+)-cysteine end groups and polyethylenimine for Cu<sup>2+</sup> is 12.7 and 13 mg g<sup>-1</sup>, respectively. The loading capacity of poly(vinyl pyrrolidinone) is 17.5 mg g<sup>-1</sup> for Cu<sup>2+</sup> and 11.9 mg g<sup>-1</sup> for Ni<sup>2+</sup>, respectively [20–23].

### 3.6. Application of the method

In order to access its effect whether the recovery of nickel is influenced by other metal ions commonly existed in real water samples, the method was applied to the recovery of nickel from binary ion mixtures. The analytical results are summarized in Table 3. Table 3 revealed that, for all fortified binary ion mixtures containing Zn(II), Ba(II), Ca(II), Mo(VI), Co(II), Cd(II), Mg(II), Mn(II) and Cr(III), the recoveries were higher than 97.6% with relative standard deviation (R.S.D.) in the range of 0.8–1.5%. Cu(II) and Pb(II) did not interfere when their concentrations existed were not more than 4.0 μg mL<sup>-1</sup>. The interference from Fe(III) can be masked by addition of 0.10 mL triethanolamine.

**Table 3**  
Recoveries of nickel from binary ions mixtures.

Mixed ions	Added (μg mL <sup>-1</sup> )		Recovery of nickel (%) <sup>b</sup>	R.S.D. (%)
	Ni(II)	Me <sup>a</sup>		
Ni(II)–Zn(II)	1.0	10.0	99.7	1.5
Ni(II)–Ba(II)	1.0	10.0	99.2	1.2
Ni(II)–Ca(II)	1.0	10.0	99.0	1.4
Ni(II)–Mo(VI)	1.0	10.0	98.6	0.9
Ni(II)–Co(II)	1.0	10.0	98.0	1.1
Ni(II)–Cd(II)	1.0	10.0	97.6	1.3
Ni(II)–Mg(II)	1.0	10.0	98.2	0.8
Ni(II)–Mn(II)	1.0	10.0	98.8	1.2
Ni(II)–Cr(III)	1.0	10.0	97.9	1.4

<sup>a</sup> The metal ions except Ni(II). Conditions: 0.50 mL 0.5% CMC, 1.00 mL of 3.0 mg mL<sup>-1</sup> KNO<sub>3</sub>, 20 mL acetone.

<sup>b</sup> Mean for five determinations.

**Table 4**  
Recoveries of nickel from various water samples<sup>a</sup>.

Samples	Found (μg mL <sup>-1</sup> )	Added (μg)	Found (μg)	Recovery of nickel (%)
Mineral water A	–	5.0	5.04 ± 0.016	100.8
Mineral water B	–	5.0	4.92 ± 0.036	98.4
Mineral water C	–	5.0	4.93 ± 0.026	98.6
Ground water	–	5.0	4.96 ± 0.022	99.2
Tap water	–	5.0	4.92 ± 0.017	98.4
Lake water	0.0225 ± 0.0065	5.0	5.08 ± 0.038	99.4

<sup>a</sup> Average of three determination ±ts/n<sup>1/2</sup> with 95% confidence.

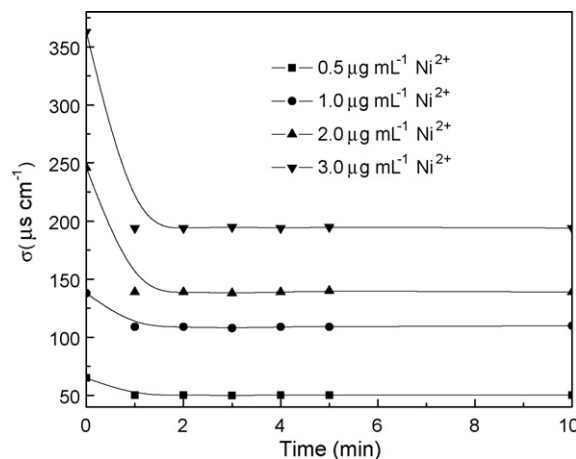


Fig. 5. Change of electrical conductivity solutions containing nickel ions and CMC polymer. Conditions: 0.50 mL 0.5% CMC.

In addition, the applicability of the proposed technique to the real water samples was investigated for mineral water, ground water, tap water and lake water samples. Depending on the concentration of nickel ions in aqueous samples, a requested pre-concentration factor could be obtained by adjusting the sample volume. However, the pre-concentration factor could not be increased as much as desired, since larger volumes could not be treated easily. In practice, sample volumes used in this study did not exceed 10.00 mL. In this case, the pre-concentration factor was 4. The calibration curve was linear in the concentration range of 0.025–3.0 μg mL<sup>-1</sup> with a correlation coefficient of 0.9993. The limit of detection was 0.019 μg mL<sup>-1</sup>. The precision of the proposed method was determined by applying the whole analytical process to 11 independent water samples spiked with 1.0 μg mL<sup>-1</sup> of nickel

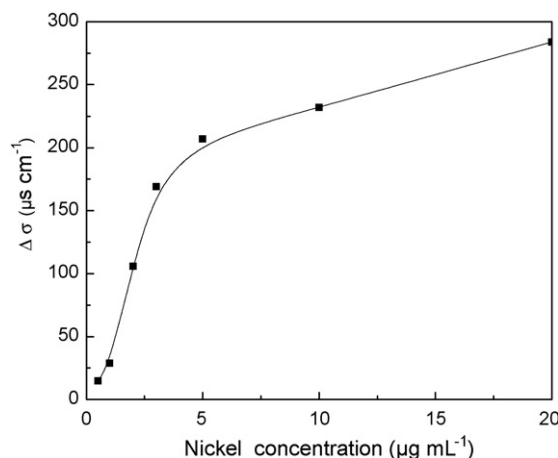


Fig. 6. Effect of nickel concentration on electrical conductivity difference. Conditions: 0.50 mL 0.5% CMC.



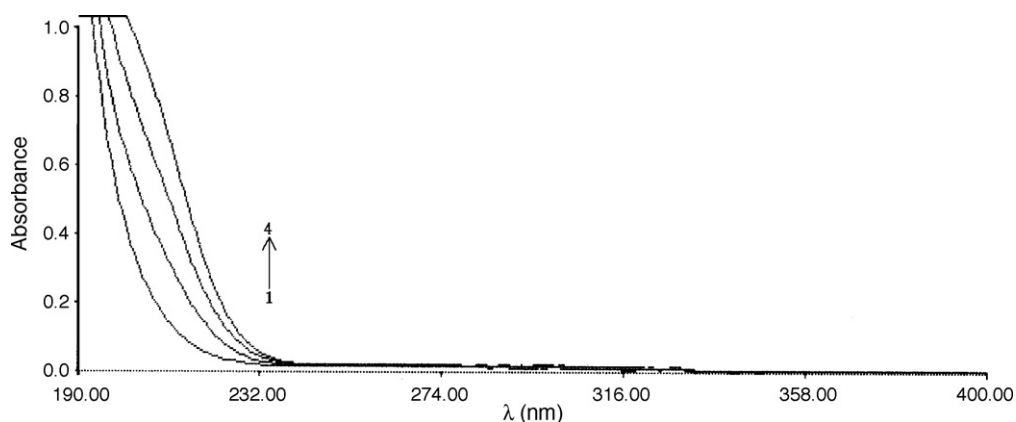


Fig. 7. UV spectra of CMC and CMC–Ni complex. “1 → 4” represents UV spectra of product formed between CMC and Ni ions in the solutions of CMC at 0, 1.0, 2.0 and 3.0  $\mu\text{g mL}^{-1}$   $\text{Ni}^{2+}$  concentration, respectively.

and the relative standard deviation (R.S.D.) was 0.73%. As demonstrated in Table 4, three mineral waters, ground water and tap water were free of nickel contamination. The concentration of nickel in the lake water was found to be  $0.0225 \mu\text{g mL}^{-1}$  and it was confirmed by spiking nickel into the lake water. The recoveries for the other spiked water samples at 5.0  $\mu\text{g}$  levels were in the acceptable range. The results demonstrated that these real water sample matrixes have little effect on the recovery of nickel.

#### 4. Mechanism of the method

The CMC–acetone system for the recovery of nickel may include the two occurring processes: (1) nickel ions are completely bound to CMC and (2) the Ni–CMC complex and free CMC molecules are precipitated in appropriate acetone. It is well known that nickel ions are not precipitated in acetone. Free CMC and CMC–Ni complex are water soluble. However, their solubility in acetone is very low [34]. As a result, free CMC molecules and CMC–Ni complexes would be precipitated in excess acetone. Hence, the formation of CMC–Ni complex is a very critical step for the CMC–acetone separation technique.

In general, interactions between water-soluble polymer and metal ions consist of various weak binding forces such as coordination bonds, hydrogen bonds, charge-transfer interaction, hydrophobic interaction, etc. These interactions are significant and act multiply and dynamically. They play an important role in the formation of polymer–metal complexes [35]. Research of Petrov and Nenov had shown that CMC possesses good complexation ability towards nickel ions where the carboxyl groups may act as a chelating ligand [17]. When CMC dissolves in water, an electrolytic process takes place to separate a CMC molecule into sodium cations and a polymer anion. All carboxyl groups existed in CMC might have had some chances to contact with the added nickel ions. Hence, when the CMC was added to the samples containing nickel ions, CMC would complex with nickel ions. In order to discuss the existence of the interactions between CMC and nickel ions, electrical conductivity and ultraviolet–visible spectra experiments of this system were studied, respectively. The results were presented in Figs. 5–7. As the results indicated, the electrical conductivity decreases significantly with the addition of the CMC polymer, compared to that of solutions only containing the same concentration of nickel ions. Furthermore, the electrical conductivity difference between the solutions only containing nickel ions and the corresponding solution containing CMC polymer and the same concentration of nickel ions increased with the increase of the initial concentration of nickel. This phenomenon can be explained by the fact that the nickel ions in aqueous solutions are easily captured by the CMC

polymer, which results in the decrease of electrical conductivity of this system. On the other hand, as shown in Fig. 7, shapes of the ultraviolet–visible spectra of CMC solutions at the presence and the absence of nickel ions have distinctly differences and the absorbance of curve increases significantly with an increase of the nickel concentration, which indicates that CMC reacts with nickel ions to form the Ni–CMC complex.

With the addition of excess acetone into the solutions, the Ni–CMC complex would be precipitated. The role of the CMC in the present method is to complex with nickel ions and form Ni–CMC complex, which can be precipitated in excess acetone. It is well known that the polymer-ultrafiltration method also requires the addition of water-soluble polymers into the aqueous solutions. However, the role of the water-soluble polymer in polymer-ultrafiltration method is to bind the metal ions to form a sufficient molecular size metal–polymer which can be concentrated by ultrafiltration for recovery or removal in a homogeneous phase. Ultrafiltration is a pressure driven membrane separation process, which requires the consumption of energy.

#### 5. Conclusions

In this work, the potential for CMC–acetone system has been demonstrated as a separation technique for the nickel recovery from water samples. From the results of our experiments, the system has been illustrated to be a simple, fast, economical technique only by mixing CMC solution with water samples and then adding acetone to the above mixtures. It is reasonable to say that the recommended CMC–acetone system for the removal and recovery of nickel from aqueous solutions is feasible in technique.

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