



Mercury (II) removal from aqueous solutions using chemically modified polyacrylamide and its copolymers

Ahmed A. H. Al-Kadhimi¹ , Asaad F. Khatab.² , Farah. Kh. H. Al-Juboory³

¹Chemistry Department / College of science / Tikrit University\Iraq

dr.ahmed4a@yahoo.com¹

²Chemistry Department / College of science / Al-Mousul University / Iraq

asaad faisal@yahoo.com²

³Chemistry Department / College of science / Kirkuk university / Iraq

farah_aljibory2003@yahoo.com³

Received date : 12 / 10 / 2015

Accepted date : 30 / 11 / 2015

ABSTRACT

Some of acrylamide copolymers were used to mercury removal from aqueous solutions of HgCl₂. The uptake capacity of these prepared copolymers was calculated.

The prepared copolymers were identified spectroscopically using infrared spectroscopy, the analysis of the resulting treated HgCl₂ solution to know the Hg (II) concentration was obtained by using atomic absorption.

Keywords: Mercury uptake; acrylamide copolymers; water treatment

إزالة ايونات الزئبق (II) من المحاليل المائية باستخدام البولي أكريل أمايد المحوّر

كيميائيا و بعض بوليمراته المشتركة

أحمد عبد الحسن أحمد الكاظمي¹ ، أسعد فيصل خطاب² ، فرح خلف حمود الجبوري³

¹ قسم الكيمياء / كلية العلوم / جامعة تكريت / العراق

dr.ahmed4a@yahoo.com¹

² قسم الكيمياء / كلية العلوم / جامعة الموصل / العراق

asaad faisal@yahoo.com²

³ قسم الكيمياء / كلية العلوم / جامعة كركوك / العراق

farah_aljibory2003@yahoo.com³

تاريخ قبول البحث: ٢٠١٥ / ١١ / ٣٠

تاريخ استلام البحث: ٢٠١٥ / ١٠ / ١٢

الملخص

تم استخدام بعض البوليمرات المشتركة لأكريل أمايد لإزالة الزئبق من المحاليل المائية لثنائي كلوريد الزئبق . و قد تم حساب قدرة امتصاص البوليمرات المشتركة المحضرة للزئبق .

شخصت البوليمرات المشتركة المحضرة باستخدام طيف الأشعة تحت الحمراء . و قد أستخدم جهاز الإمتصاص الذري لقياس تركيز ايونات الزئبق في محاليل ثنائي كلوريد الزئبق الناتجة بعد المعاملة مع البوليمر .

الكلمات الدالة: امتصاص الزئبق ، بوليمرات مادة الأكريلاميد ، معالجة المياه .

1. Introduction

From different industrial heavy metal wastes, mercury is among those with the greatest impact on environment. Removal of mercury from aqueous solution is of special importance in waste water treatments and in hydrometallurgical applications. Removal of trace mercury can not be achieved by conventional ion exchangers. Removal of mercury and other toxic metals require

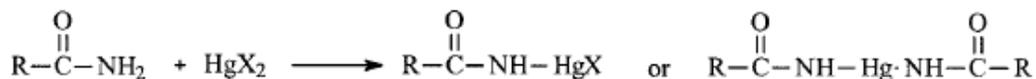
more efficient sorbents. Specially designed chelating polymers show excellent metal-uptake capabilities and these have been discussed in many articles and reviews.[1,2]

However, most of those polymeric sorbents do not show desired selectivity, especially when multi-component mixtures are in question. Selective extraction of any desired metal ion is important not only for the isolation or removal of one chemical component but also for the effectiveness of the sorbent material because, during the extraction of any metal ion targeted, a waste amount of ligating groups should be spent for the extraction of common abundant metal ions such as Ca(II) and Mg(II) at the same time. In that case, only a few percent of the ligating groups of the sorbent serve in the removal of a target chemical, and this greatly reduces the effectiveness of the sorbent. In some cases, selective metal ion removal can be achieved to some extent by the proper choice of conditions, such as pH adjustment.[3,4,5]

Ideally, the best method of selective separation is to find a suitable ligating group that is selective only for the target metal ion and not for any other metal ions. However, this is impossible in practice because most chelating groups show, more or less, coordination tendencies to many metal ions.

However, there are a few exceptions, such as mercury ions with superior affinity toward thiol, thioether, and amide groups. According to this principle, a number of mercury selective polymer resins with thiol[6]or thioether functions[7]have been reported. Nevertheless, those materials presented are not strictly selective and also sorb other metal ions such as Pb(II) and Cu(II) to some extent.[8]

Another possibility of selective mercury extraction is to use polymer resins with amide groups. The chemistry of mercury–amide interactions has been known for about 100 years. Amide compounds readily react with mercuric ions, under ordinary conditions, to give monoamido–mercury or diamido–mercury compounds as shown bellow[9]:-



The mercury–amide linkage is believed to be covalent rather than coordinative.[9]

The amide group, however, is a weak donor because of an electron-withdrawing carbonyl group. Therefore, it shows very little tendency for coordination with transition-metal ions. This makes amide groups unique in mercury binding with extremely high selectivity. On the basis of this key principle, we had demonstrated that acrylamide copolymers are able to bind mercury selectively.

2. Experimental Part

2.1. Materials and instruments

All the chemicals used have been supplied by Fluka and Aldrich.

Infrared spectra have been recorded by shemadzue FT-IR-8400 s Fourier transform, in the range between ($4000-400\text{ cm}^{-1}$), Varian-AA-240FS Fast Sequential Atomic Absorption Spectroscopy/ Australian used for measuring the concentration of Hg(II) ions in aqueous solutions and all the samples have been dried under reduced pressure at 65-75 C°.

2.2.Preparation of Polyacrylamide (A-1)

(4.0000 g.) of the monomer (acrylamide) was dissolved in a mixture of toluene (30 ml) and methanol (10 ml) in a round bottom flask and then added to the reaction mixture (0.0200 g.) of the initiator (dibenzoyl peroxide). The reaction mixture was refluxed in a water bath at (75 C°) with constant stirring for 30 minutes. The polyacrylamide was filtered and washed well with a mixture of toluene and methanol several times. The weight of product after drying was (2.9800 g).

2.3.Hydrazinolysis of Polyacrylamide (A-2)

(1.0000 g.) of the polyacrylamide was dissolved in a (1 ml) of distilled water (polyacrylamide solution 50% wt.), then (2 ml.) of hydrazin hydrate (35%) was added to the reaction solution. The reaction mixture was refluxed with constant stirring for (3 hrs.).

After cooling a little ethanol was added to precipitate the polymeric product, then the resulting mixture was filtered and washed with a little ethanol. The weight of product after drying was (1.3476 g.).

2.4.Preparation of Polyxanthylacrylamide (A-3)

(0.2500 g.) of Xanthhydrol was dissolved in (3.5 ml.) of glacial acetic acid; an oil was separated (as is sometimes the case with commercial material), allowed to settle for a short time

and the supernatant solution was decanted, then (0.2500 g.) of polyacrylamide was added, shaken and allowed to stand. The reaction mixture was refluxed in a water bath at (60 C°) with constant stirring for (2 hrs.).

A viscous liquid was obtained, after cooling a little methanol was added, the resulting mixture was filtered and the precipitate was washed off with distilled water several times and with a little methanol. The weight of product after drying was (0.3291 g.).

2.5.Nitration of Polyxanthylacrylamide (A-4)

(3.68 ml.) of concentrated nitric acid was mixed with (4 ml.) of concentrated sulphuric acid in round bottomed flask in ice bath. Then, (0.2500 g.) of polyxanthylacrylamide was added. The reaction mixture was refluxed in a water bath at (70 C°) with constant stirring for (3 hrs.) and the resulting mixture poured into a (75 ml.) of water. The polymer was collected and washed with excess of water several times until the removal of acidity and washed with methanol. The weight of product after drying was (0.2729 g.).

2.6.reparation of Poly(acrylamide-co-styrene) (A-5)

(0.5000 g.) of acrylamide and (0.5000 g.) was dissolved in (3 ml.) of DMF in a round bottom flask and then (0.0100 g.) of the initiator (dibenzoyl peroxide) was added. The reaction mixture was refluxed in a water bath at (75 C°) with constant stirring for (3 hrs.). The reaction mixture was added to (150 ml.) of cold water, the copolymer was filtered and dried. The weight of product after drying was (0.5564 g.).

2.7.Copolymerization of Acrylamide and N-vinylcarbazole (A-6)

(1.5000 g.) of acrylamide and (1.5000 g.) of N-vinylcarbazole were dissolved in a mixture of toluene (23 ml) and methanol (7 ml) in a round bottom flask and then added to the reaction mixture (0.0150 g.) of the initiator (dibenzoyl peroxide). The reaction mixture was refluxed in a water bath at (75 C°) with constant stirring for 30 minutes.

The copolymer was filtered and washed well with a mixture of toluene and methanol several times. The weight of product after drying was (1.4509 g).

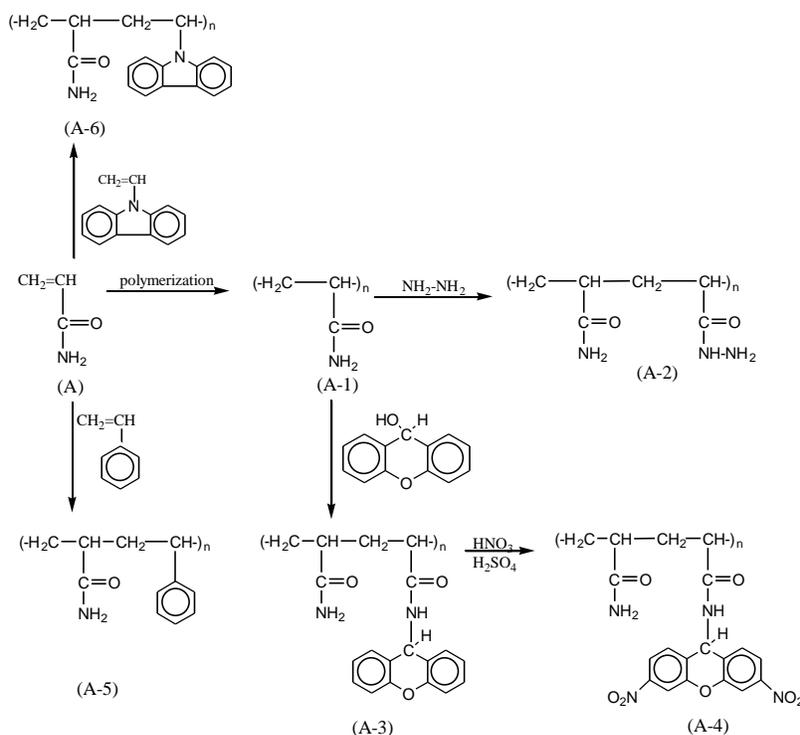
2.8.Mercury Removal

The mercury sorption capacities of the grafted polymers with acrylamide were determined by mixing weighted amount of copolymers (0.1 g.) with (10 ml.) aqueous Hg (II) solution (0.1 M).

The mixture was stirred for (4,8,12,16,20 and 24) hrs. and then filtered. The Hg (II) concentrations were determined by atomic absorption.

The mercury loading capacities of acrylamide copolymers were calculated from the initial and final Hg (II) contents of the solutions.

3. Results and Discussion



Scheme (1): Expected chemical structure of modified polymers prepared from acrylamide.

3.1. Preparation of Polyacrylamide (A-1)

In this study linear polyacrylamide was prepared by free radical polymerization of acrylamide using dibenzoyl peroxide as a radical initiator.

In the infrared spectrum of polyacrylamide, the two strong intensity bands appearing around 3386 cm^{-1} and 3199 cm^{-1} are undoubtedly associated with the N-H stretching vibrations. The corresponding modes in acrylamide are found at 3352 cm^{-1} and 3180 cm^{-1} . The methylene group vibration useful to monitor the extend of polymerization. The calculated values 2933 cm^{-1} and 2864 cm^{-1} are assigned to asymmetric and symmetric CH_2 stretching vibrations, respectively.

In acrylamide (the monomer), these modes are observed at 3105 cm^{-1} 3030 cm^{-1} . The lowering of the above frequencies in polyacrylamide compared to acrylamide is mainly due to the unsaturated linkage in monomer acrylamide. The weak intensity infrared band observed at 2786 cm^{-1} in polyacrylamide has been assigned to CH stretching mode.

3.2. Hydrazinolysis of polyacrylamide (A-2)

Hydrazinolysis is a chemical cleavage reaction in which the hydrazine $\text{NH}_2\text{-NH}_2$ acts as a nucleophilic agent by attacking a carbonylic carbon. Hydrazinolysis of aqueous 50% w/w polyacrylamide in water by refluxing for (3 hrs.) with aqueous hadrazine (35%) yielded the poly (acrylic hydrazide-co-acrylamide). The product was precipitated by the addition of an equal volume of ethanol.

Treatment with hydrazine hydrate modifies nonreactive amide groups in the polyacrylamide to hydrazide groups, as shown in scheme-1.

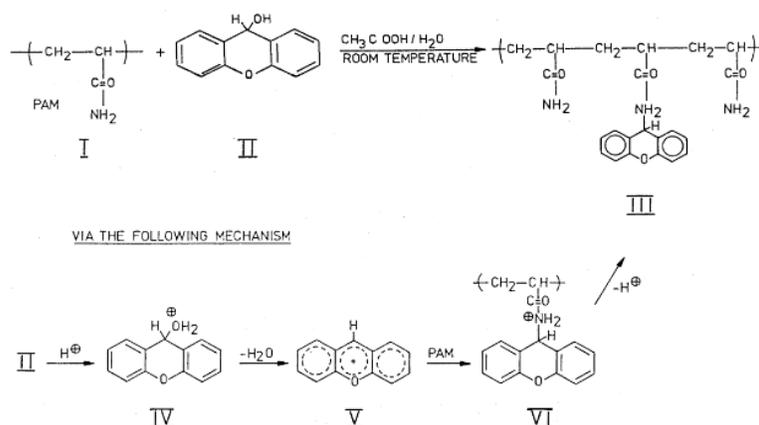
In the infrared spectrum of poly(acrylic hydrazide-co-acrylamide), the copolymer has two bands, at 3448 cm^{-1} and 3174 cm^{-1} which have been ascribed to the asymmetric and symmetric NH_2 stretching vibrations. The copolymer has a band at 3386 cm^{-1} which has been ascribed to the NH stretching vibration. It has a sharp band at 1629 cm^{-1} ascribed to the C=O stretching vibration and the 1589 cm^{-1} band ascribed to the NH_2 bending vibration.

The copolymer has three bands, at 1444 cm^{-1} , 1388 cm^{-1} and 1344 cm^{-1} due to the NH_2 or NH deformation vibrations, these bands are taken as characteristic of the $-\text{CONHNH}_2$ group.

3.3. Preparation of Polyxanthylacrylamide (A-3)

Water soluble, amide group containing polymers such as polyacrylamide are modified, by reacting the polymer in aqueous solution with organic dye molecules which can form stable carbo-cations.

One of the most preferred dye molecules is xanthhydrol. A preferred embodiment of this reaction will be further described, by way of illustration only, with reference to scheme-2 which depicts a mechanism for forming a labeled polymer from polyacrylamide and 9-xanthhydrol.[10]



Scheme (2): Mechanism for forming polyxanthylacrylamide^[10]

As can be seen in scheme-2 polyacrylamide indicated by numeral (I) is reacted with 9-xanthhydryl, indicated by numeral (II) to produce labeled polyacrylamide (III). The mechanism is shown below the overall reaction, and includes the steps of first protonating the 9-xanthhydryl (II) to give the intermediate (IV), which is dehydrated to form the intermediate (V). This intermediate reacts at the amide nitrogen of (I) to give the intermediate (VI) results in the labeled polymer (III).

In the infrared spectrum, the copolymer has a band at 3458 cm^{-1} and 3336 cm^{-1} which have been ascribed to the asymmetric and symmetric NH stretching vibrations. It has a sharp band at 1658 cm^{-1} ascribed to the C=O stretching vibration and the 1606 cm^{-1} band ascribed to the NH bending vibration. IR spectrum of the resultant copolymer showed absorption of C-C stretching in rings of xanthene group at 1454 cm^{-1} , C-O stretching vibration at 1336 cm^{-1} .

3.4.Nitration of Polyxanthylacrylamide (A-4)

Nitrated polyxanthylacrylamide was obtained by the nitration of polyxanthylacrylamide using a mixture of concentrated nitric acid/concentrated sulfuric acid, as shown in scheme-1.

The IR spectrum of nitrated polyxanthylacrylamide showed absorption of N=O asymmetric stretching at 1537 cm^{-1} , and N=O symmetric stretching at 1350 cm^{-1} .

3.5.Preparation of Poly(styrene-co-acrylamide) (A-5)

Poly(styrene-co-acrylamide) was synthesized by free radical polymerization of a mixture of styrene and acrylamide in DMF, by using dibenzoylperoxide as an initiator. In copolymer spectra, there are characteristic and intense peaks found at 3348 cm^{-1} , 1676 cm^{-1} and 1026 cm^{-1}

indicating the N-H stretching , C=O stretching and C-N stretching due to acrylamide group. In addition, the peak at 1606 cm^{-1} band represents the bending of the weak bond N-H.

3.6.Copolymerization of Acrylamide and N-vinylcarbazole (A-6)

Poly(acrylamide-co-N-vinylcarbazole) was synthesized by free radical polymerization of Acrylamide and N-vinylcarbazole in a mixture of toluene and methanol, by using dibenzoylperoxide as an initiator.

In the infrared spectrum of poly(acrylamide-co N-vinylcarbazole), there are shifts occurs in the vibrations as we can see from copolymer. The vibration for hydrogen bonded NH group in this copolymer has been approximately shifted to 3382 cm^{-1} from 3386 cm^{-1} , whereas the band corresponding to C=O has been blue shifted to 1668 cm^{-1} from 1672 . The bending vibration band of NH has been blue shifted to 1330 cm^{-1} from 1348 cm^{-1} . The above observations clearly indicate the composite formation during the synthesis process.

3.7.Mercury Removal

Acrylamide copolymers (A-2), (A-3), (A-4), (A-5) and (A-6) were used to Hg(II) removal.

Mercury binding via amide groups in principle can occur either by formation of monoamide or diamide mercury structures, which provide a means of capturing Hg^{2+} from aqueous solution.

Aqueous solution of HgCl_2 was used in mercury sorption experiments. The absorption capacity of the copolymers that contain amide groups was analyzed by the determination of the excess mercury ions in the supernatant solution. The mercury sorption capacity of poly(styrene-co-acrylamide) and poly(acrylamide-co-N-vinylcarbazole) from $(0.1\text{ M})\text{ Hg}^{2+}$ is given by:-

$$(M_0 - M) \times V / Wt.$$

The relevant data are listed in Tables (3-1), (3-2), (3-3), (3-4) and Table (3-5).

Table (3-1): (A-2) capacity of mercury uptake

Time (hrs.)	[Hg ²⁺] (M)	Copolymer Capacity of mercury uptake (mmol.g ⁻¹)
0	0.100	0.0
4	0.092	0.8
8	0.086	1.4
12	0.070	3.0
16	0.067	3.3
20	0.045	5.5
24	0.043	5.7

Table (3-2): (A-3) capacity of mercury uptake

Time (hrs.)	[Hg ²⁺] (M)	Copolymer Capacity of mercury uptake (mmol.g ⁻¹)
0	0.100	0.0
4	0.098	0.2
8	0.095	0.5
12	0.088	1.2
16	0.079	2.1
20	0.072	2.8
24	0.072	2.8

Table (3-3): (A-4) capacity of mercury uptake

Time (hrs.)	[Hg ²⁺] (M)	Copolymer Capacity of mercury uptake (mmol.g ⁻¹)
0	0.100	0.0
4	0.100	0.0
8	0.097	0.3
12	0.092	0.8
16	0.088	1.2.
20	0.087	1.3
24	0.085	1.5

Table (3-4): Poly (styrene-co-acrylamide)(A-5) capacity of mercury uptake

Time (hrs.)	[Hg ²⁺] (M)	Copolymer Capacity of mercury uptake (mmol.g ⁻¹)
0	0.100	0.0
4	0.089	1.1
8	0.077	2.3
12	0.064	3.6
16	0.049	5.1
20	0.041	5.9
24	0.037	6.3

Table (3-5): Poly (acrylamide-co-N-vinylcarbazole) (A-6) capacity of mercury uptake

Time (hrs.)	[Hg ²⁺] (M)	Copolymer Capacity of mercury uptake (mmol.g ⁻¹)
0	0.100	0.0
4	0.087	1.3
8	0.075	2.5
12	0.061	3.9
16	0.046	5.4
20	0.038	6.2
24	0.033	6.7

References

- [1] S.D. Sahni and J. Reedijk, *Coord. Chem. Rev.*, 59,1 , (1984).
- [2] B. L. Rivas and K. E Geckeler, *Adv. Polym. Sci.*, 102, 171, (1992).
- [3] Wagner, C. K., Hall, G., Rigel, B., Virgilio J. D. and Kamath V., *Germann, G. J Appl. Polym. Sci.*, 31, 1797, (1986).
- [4] B. L. Rivas, H. A. Maturana, I. M. Perich, U. Angne, *Polym. Bull (Berlin)*, 14, 239, (1985).
- [5] M. Luhrmann, N. Stelter, A. Kettrup, *Anal. Chem.*, 322, 2337, (1985).

- [6] M. C. Dujardin, C. Caze` and I. Vroman, *React Funct Polym*, 43, 123, (2000).
- [7] K. Yamashita, K. Kurita, K. Ohara, K. Tamura, M. Nango and K. Tsuda, *React. Funct. Polym.*, 31, 47, (1996).
- [8] A. Lezzi, S. Cobianco and A. Roggero, *J. Polym. Sci., Part A: Polym. Chem.*, 32, 1877, (1994).
- [9] H. B. Sonmez, B. F. Senkal and N. Bicak, *Journal of Polymer Science: Part A: Polymer Chemistry*, 40, 3068–3078 (2002).
- [10] H. B. Sonmez and N. Bicak, *Reactive & Functional Polymers*, 61, 33-41, (2004).

AUTHOR



Ahmed A. H. Al-Kadhimi: received B.Sc. and M.S. degrees in Chemistry from, College of Science/Baghdad University/Baghdad-Iraq in 1975 and 1977, respectively. In 1985 received Ph.D. in Organic Chemistry from Lancaster University-U.K. At 1999 till 2003 as a head of Chemistry Department in the College of Science/ Tikrit University and ead of scientific promotion committee in the College of Science/ Tikrit University for the period between 2006-2010. At 2010 till now as Senior Lecturer in Chemistry Department, College of Sciences, Tikrit University.