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THE CHEMISTRY AND PROPERTIES OF POLY(ACRYLAMIDE-ACRYLIC ACID) RESINS

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Key Words: Radiation Polymerization, Template Polymerization, Polymerization of Acrylic Acid, Acrylamide Polymeric Resins, Waste Treatment

ABSTRACT

Acrylamide polymeric resins such as: poly(acrylamide-acrylic acid p(AM-AA), poly (acrylamide-acrylic acid-diallylamine hydrochloride p(AM-AA-DAA)^{+Cl})] and poly(acrylamide-acrylic acid-diallylethylamine hydrochloride) p[(AM-AA-DAEA)^{+Cl}] were prepared by gamma radiation-initiated template polymerization of acrylic acid on acrylamide polymers. Copolymerization of acrylic acid with acrylonitrile produce poly(acrylic acid-acrylonitrile) p(AA-AN) resin. The capacities of the prepared polymeric materials were investigated at different doses. The results showed that the maximum experimental capacities are similar to their theoretical values. The chemical stability of the polymeric materials were investigated at different

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pH-values. The mechanism of interaction between the functional groups of the polymeric chains and ions in aqueous solution were studied. The polymeric materials have extraordinary capacities and were used as good exchangers in the treatment of wastewater for removal of metallic ions from their aqueous solutions.

INTRODUCTION

The polymeric materials, having polyfunctional groups such as carboxylic amide-, nitrile- and ammonium groups will possess good hydrophilic properties, as well as good ion-exchange properties. These polymeric materials were used for removal of metallic ions such as: Cu^{2+} , Fe^{2+} , Zn^{2+} and Mg^{2+} from wastewater and were also used in the treatment of radioactive liquid waste containing radioactive isotopes such as Cs^+ , Co^{2+} , Sr^{2+} and Eu^{3+} [1-12].

The polymeric materials were prepared by ionizing radiation and chemical initiators using different polymerization techniques such as: copolymerization, template polymerization and grafting polymerization. These polymeric materials were prepared in different forms such as water-soluble polymers, hydrogels and resins depending on the technique which was used. The physical and chemical properties of the polymers were found to be dependent on the nature of monomers and conditions of their polymerization such as: radiation dose, dose-rate, monomer concentration and the nature of polymerization medium. The aim of this work, the chemistry and the properties of the polymeric materials such as polymerization technique, the capacities of the polymeric materials and possible mechanisms for interaction of the active functional groups of the polymeric chains with ions in aqueous solution were investigated.

EXPERIMENTAL

Preparation of Polymers

Water-soluble polymers and polymeric gels such as [13-17]: PAM, P(AM-DAA-HCl), P(AM-DAEA-HCl), and P(AA-AN) resin were prepared by gamma radiation initiated copolymerization of the corresponding monomer solutions.

Polymeric resins such as: P(AM-AA), p[(AM-AA-DAA)⁺ Cl⁻], and p[(AM-AA-DAEA)⁺Cl⁻] were prepared by template polymerization of acrylic acid on the prepared polymers [7-9].

Capacity Determination

The investigated resin was treated with 0.1N NaOH to pH~7 to neutralize the acidic groups in the polymer. The treated resins were added to the solution of copper sulfate (0.04M) and the mixture was agitated. After settlement of the solution, the percent of the uptake of the resin for Cu²⁺ was determined spectrophotometrically.

The capacity in m mol/g of the resins was determined using Equation 1 [5].

$$C = \frac{\% \text{ uptake}}{100} \times \frac{C_0 \times V}{m} \quad (1)$$

where : C₀ is the initial concentration of the solution (mol/L),
 V is volume of the solution, ml, and
 m is the weight of the added polymer, g.

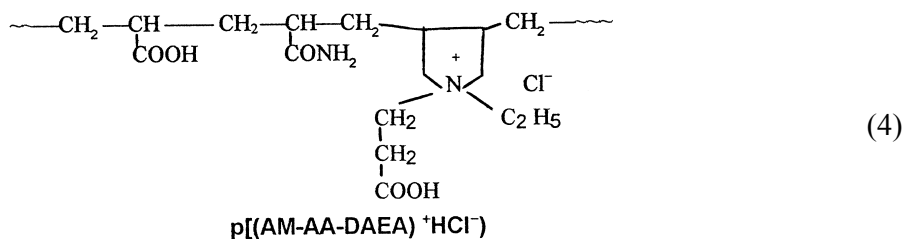
RESULTS AND DISCUSSION

The polymeric resins such as poly(acrylamide-acrylic acid) p(AM-AA), poly(acrylamide-acrylic acid-diallylamine-hydrochloride). p[(AM-AADAA)⁺Cl⁻] and poly(acryl-amide-acrylic acid-diallylethylamine-hydrochloride p[(AM-AA-DAEA)⁺Cl⁻] were prepared by a template polymerization of acrylic acid on acryl-amide polymers [5, 7-9].

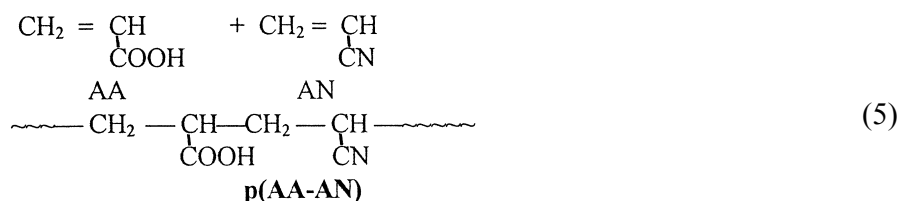
The propagation reactions in the template polymerization attributed to the possible steps [18, 19]:

(a) propagation of the monomer by the generated free radicals from the monomer, the polymer and the solvent and

(b) the propagation of the monomer associated with the polymer by the free radicals generated in the system to form polymer complexes. Consequently, the reaction mechanism can be written as (Equations 2, 3, and 4):



Poly(acrylic acid-acrylonitrile) resin p(AA-AN) was prepared by gamma-irradiation initiated copolymerization of acrylic acid (AA) with acrylonitrile (AN) in aqueous solution according to Equation 5 [11].



The spectroscopic studies [7, 8] of p[(AM-AA-DAA)⁺Cl⁻] does not show any absorption bands due to >NH stretching vibration of amine salts. This indicates the absence of hydrogen atom of >NH in the polymeric chains. This can be attributed to the addition of acrylic acid on the ammonium groups of p(AM-DAA-HCl) and p(AM-DAEA-HCl), as shown in Equations 3 and 4, respectively.

The addition of the monomer on ammonium groups converts chain ends of the ammonium groups in the added copolymer into acrylic units in the obtained resin. Accordingly, the probability of the polymer degradation decreases [20]. This can be attributed to these chain ends of acrylic units are more stable to irradiation than ammonium groups [21].

Capacity Determination

The theoretical capacity for polymeric materials can be calculated on the basis that two repeating units which contains the active functional groups such as: -CONH₂, -COOH and -CN can react with divalent metallic ions such as Cu²⁺ to form a crosslinked structure after cation build-up as discussed in Equation 6.

$$\text{The theoretical uptake} = \left(\overline{X}_o \right) \times 100 \quad (6)$$

where: X is the weight of Cu^{2+} equivalent to the weight of added resin.
 X_0 is total weight of Cu^{2+} per added volume of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

The theoretical capacity was calculated according to Equation 1.

The theoretical and experimental capacities for different polymeric materials were determined as given in Table 1. The deviation of theoretical capacities (C_{theo}) from their experimental values [5, 7-11] (C_{exp}) was calculated as follows:

$$D1 = \frac{C_{\text{theo}} - C_{\text{exp}}}{C_{\text{theo}}}$$

and

$$D2 = \frac{C_{\text{exp}} - C_{\text{theo}}}{C_{\text{exp}}}$$

Table 1 shows that the values of the experimental and theoretical are near to each other. The deviation can be attributed to the experimental error. This means that the polymeric materials have an extraordinary capacity toward cations, and it can be used as good exchangers for treatment of wastewater.

The capacities of the resins toward Cu^{2+} were determined at different doses, and the results are given in Table 2. The results show that the capacity increases with increasing the radiation dose. This can be attributed to increasing the degree of crosslinking between the polymeric chains due to irradiation [22-24]. The decrease in the capacity may be attributed to higher increase in the

TABLE 1. Capacities for Polymeric Materials

Polymeric Materials	Capacity, m mol/g			
	Theoretical	Experimental	D1	D2
p(AM-AA)	7	7.5	7.5	0.06
p(AA-AN)	7.3	7.4	7.4	0.013
p[(AM-AA-DAA) ⁺ Cl ⁻]	6.44	6.37	6.37	0.01
p[(AM-AA-DAEA) ⁺ Cl ⁻]	6.82	7.16	7.16	0.05

extent of crosslinking [25-26] and decreasing the number of carboxylic groups [24]. In addition, the number of amide groups decreases due to imidation of amide groups [23, 27].

Chemical Stability of the Resin

The release percent of Cu^{2+} from the solid phase which formed from interaction of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ with P(AM-AA) resin determined spectrophotometrically at different pH-values. The results are shown in Table 3, which shows that the release percent of Cu^{2+} decreases with increasing the pH-values. The release percent is zero at $\text{pH} > 5$. This may be due to the effect of pH on the function groups of the resin as discussed in the following [11].

At low pH, the amide groups of acrylamide unit are mostly in the protonated form leading to imidation of amide groups and the formation of intermol

TABLE 2. Influence of Doses on the Capacities of Polyacrylamide Resins Tower Cu^{2+}

Dose kGy	[p(AM-AA- DAA)+Cl]	Capacity m mol/g		
		[p(AM-AA- DAEA)+Cl-]	p(AM-AA)	p(AA-AN)
1.68	4.15	3.8	-	-
3.0	-	-	-	5.8
5.0	4.50	4.0	-	-
8.4	5.44	6.15	-	-
9.0	-	-	-	6.8
11.76	-	-	6.3	-
16.8	6.37	7.16	-	-
25.2	5.9	-	-	-
30.0	-	-	5.1	7.4
42.0	-	-	7.5	-
50.0	4.44	5.14	-	-
57.12	-	-	6.15	-
60.0	-	-	-	6.8
84.0	-	-	5.5	-
120	-	-	-	6.2

TABLE 3. Influence of pH on the Release Percent of Cu^{2+}

pH	Release Percent
.25	92.5
3.74	78.5
4.70	26.0
5.00	0
6.5	0

ecular crosslinking between polymeric chains [28, 29]. By increasing the pH, the degree of protonation and imidation of the amide groups decreases, this leads to increasing the probability of formation of complexes between the amide groups and the metal ions.

At low pH, the carboxylic groups of acrylic acid unit are also mostly present in nonionized form. Consequently, no interaction can occur between the carboxylic groups and the metal ions. On increasing the pH-value, the carboxylic groups are ionized and spaced along the polymeric chains (30-32). This leads to an increase in the probability of interaction between the carboxylic groups, and metal ions might be present in the solution.

Mechanism of Interaction Between Polymers and Ions in Aqueous Solution

The spectroscopic studies [5-12] for the polymeric materials after cation build-up, as a result of interaction between polymers such as: Polyacrylamide p(AM), Poly(acrylamide-acrylic acid) p(AM-AA), Poly(acrylamide-diallylamine-hydrochloride), p(AM-DAA-HCl), poly (acrylamide-diallyl-diethylammonium chloride) p(AM-DADEAmCl), poly(acrylamide-sodium acrylate-dialldiethyl-ammonium chloride) p(AM-AANa-DADEAmCl) and poly(acrylic acid-acrylo-nitrile) p(AA-AN) with copper sulfate are summarized in Table 4. The data of Table 4 shows that:

(1) The presence of the absorption band characteristic for chelate compound may be due to complex formation between neutral groups such as: amide group- CONH_2 and nitrile group-CN with Cu^{2+} . This is in agreement with the findings of other authors (32-36) in interaction. of polyacrylamide, poly(4-vinylpyridine) PVP, poly(ethyleneimine) PEI, poly(vinylimiazole) PVI, poly(ethylenepyridine-2-aldiamine), poly-(vinyl-amine), poly(amido-amine),

TABLE 4. Absorption Bands of Acrylamide Polymers with Copper Sulfate, cm^{-1}

Groups	p(AM)	p(AA-AN)	p(AM-AA)	p(AM-DAA-HCl)	p(AM-DADEAmCl)	p(AM-AANa-DADEAmCl)
Amides II: Free >NH stret., 3500, 3400	3390		3482	3359	3415	3439
Bonded >NH stret, 3350, 3180 >NH bend. 1620- 1590	3270		3304 1619		1616, 1576	1558, 1540
amide I > C=O stret., 1650	1651			1654	1646	1653
Aliphatic: CH ₂ stret. 2960 - 2870 CH ₃ bend, 1380, 1460, 1420 CH ₂ bend, 1300-1100, 1470-1400, 740 - 720	2965 1485	1489 1472	2968	2923 1519-1450	1489, 1472, 1457, 1418	1472, 1457 1418
Carboxylate: -COO ⁻ stret., 1610-1550 -COO ⁻ bend 1400-1300		1616 1558 1418	1565 1419			1558 1418
Ester: > C=O stret., 1750-1735		1733	1739			1771 1731
Amine: CN stret., 1410 > NH stret: 3000-2700 & 2700-2500				1427	1418	1418
-C≡N stret.: 2400-2200		2360				
Chalet compounds: 3200-2400		2360		3243	2360	2361
Ionic sulfate: 480 - 400 1140-1170				1110, 497	1118, 482, 458	1118, 480

poly(N,N,N',N'-tetramethyl-ethan-1,2-diamine), 4-and polydioximes with cations such as Cu, Ni, Cd, Fe, Cr and Hg.

(2) The presence of the absorption bands characteristic for COO⁻ can be attributed to cation-exchange between-COOH/-COONa with Cu²⁺ [1-12].

(3) The absence of the absorption band characteristic for > NH stretching can be attributed to cation-exchange between H⁺ of ammonium group and Cu²⁺ [1-12].

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