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SYNTHESIS POLY(HYDROXAMIC ACID) BY MODIFICATION OF POLYACRYLAMIDE HYDROGELS WITH HYDROXYLAMINE HYDROCHLORIDE AND APPLICATION FOR ADSORPTION OF La(III), Pr(III) IONS

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Abstract

Poly(hydroxamic acid) (PHA) was synthesised by modification of polyacrylamide hydrogels with hydroxylamine. Some effects such as temperature, time, hydroxylamine hydrochloride concentrations and pH on hydroxamic acid functional groups were studied. The results showed that hydroxamic acid functional groups in polymer is the highest in following conditions: 30 ^oC temperature; 24 hour, 3.3 M $NH_2OH.HCl$ concentrations and pH = 14. Beside, PHA was characterized by fourier transform infrared spectroscopy (FTIR) and scanning electron microscope (SEM). PHA were also applied for adsorption of La(III) and Pr(III) ions. The adsorption of La(III) and Pr(III) ions on poly(hydroxamic acid) conformed to linear form Langmuir adsorption isotherm, maximum capacities for La(III), Pr(III) were found as 234.19 and 209.64 mg/g at pH = 6, respectively.

Keywords. Poly(hydroxamic acid), adsorption, ion-exchange, Praseodymium, Lanthanum.

I. INTRODUCTION

Rare earth metals (REMs) are active elements. It is applied widely in metallurgy, petrochemical industry, laser materials, glass ceramic field, refinement of microstructure, alloying, laser materials, high temperature superconductors and purification of materials…[1, 2]. Many methods had been used for the extraction process and purification of REMS such as filtration, liquid-liquid extraction, solid-liquid extraction, ion-exchange, electro winning, etc… [3, 4]. Therein, the method using ion-exchange resin are applied for separating REMs with high purity.

In recent year, ion-exchange resins have been used to separate and reclaim of (REMs) based on hydroxamicaxit (-CONHOH) functional groups received attention of the scientific community. Selvi et al [5] studied using poly(hydroxamic acid) (PHA) to separate gallium(Ga) from sodium aluminate liquor. Khaled F, Hassan et al [6] reported the using PHA to separate Zr from Zr/Y, Sr systems. Mohamad Zakiet al [7] studied PHA for extraction of lanthanide group elements from aqueous media. Md. Jelas Haron [8] synthesized of poly(hydroxamic acid) from cross-linking poly(methacrylate) and characterized their behaviors. M. R. Lutfor [9] studied on synthesis and characterization of poly(hydroxamic acid) chelating resin from poly(methyl acrylate)-grafted sago starch.

In this paper, the synthesis of PHA by modification process of polyacrylamide with hydroxylamine hydrochloride and effects of temperature, time, hydroxylamine concentrations, pH on hydroxamic acid functional group content sand characterization of poly(hydroxamic acid) were studied. Beside, PHA were also applied for adsorption of La(III) and Pr(III) ions. The adsorption of La(III) and Pr(III) ions on poly(hydroxamic acid) conformed to linear form Langmuir adsorption isotherm.

2.EXPERIMENTAL

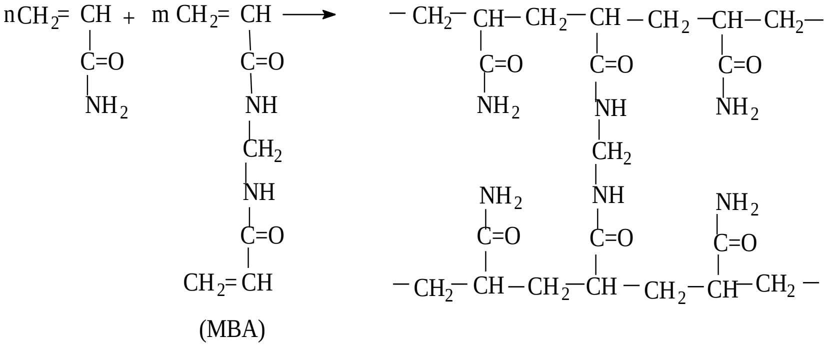
2.1. Materials

Acrylamide (AM) > 99 % (Merck, Germany), *N,N'*- metylene-bis-acrylamide (MBA) purity > 99 % (Sigma), ammonium persulfate $(NH_4)_2S_2O_8$ (APS) > 99 % (Merck, Germany), hydroxylamine hydrochloride NH_2OH. HCl, purity > 98.5 % (Sigma), standard solution of $La(NO_3)_3$ concentration 1000 mg/l (Merck), $Pr(NO_3)_3$ concentration 1000 mg/l (Merck), liquid parafin: density 0.845 g/ml, span 80 (China), HCl: 38% (China), NaOH: 99 % (China), ethanol 96^o (VN), distilled water (VN).

2.2. Polymer preparation and characterization

2.2.1. Preparation of polyacrylamide by inverse suspension polymerization

Mixture of paraffin liquid with span 80 surfactant (a ratio of span/paraffin = 0.1 wt%) was poured into the flask and heated up to 75 °C. A solution consisting of 30 wt% acrylamide, 1 wt %, ammonium persulfate (APS) initiator and 7 wt% MBA cross-linking concentration. After then this solution was dropped into the flask at speed of 10 g/min that helped to remain reaction temperature stability. Maintain stirring speed at 300 rpm/min for 240 minutes until the polymerization take place completely. Finally, the reaction mixture was cooled down to room temperature while stirring. Then filtered to remove paraffin liquid. Polymer was washed several times with hot water, distilled water and ethanol-water solution before drying in a vacuum at 70 °C. The schematic representation of acrylamide synthesis is shown in scheme 1.



Scheme 1: Synthesised reaction of polyacrylamide

2.2.2. The modification process of polyacrylamide with hydroxylamine hydrochloride

30 ml $NH_2OH.HCl$ solution with various concentrations was added to 0.5 g polyacrylamide hydrogels in 100ml distilled water. The resulting mixture was stirred at relevant temperature, maintain stirring speed at 100 rpm/min followed by addition of 1.5 M NaOH to pH at 11, 12, 13, 14, respectively. The reaction was continued for 24 hour at room temperature. Ammonia was liberated during the reaction. The resulting polymer was washed with distilled water and acidified with 1M HCl solution then washed with distilled water until chloride–free. Polymer dried in a vacuum at 70 °C.

2.2.3. Adsorption process of La(III), Pr(III) ions

The adsorption capacities were obtained from the exchange of the dry PHA polymer (0.15 g) with 50 ml of 500 mg/l $La(NO_3)_3$ or $Pr(NO_3)_3$ solution at pH = 6 for 4 hours on magnetic stirrer at 30 °C with constant speed. The adsorption capacities were determined from the decrease in La(III) or Pr(III) ion concentration in solution after equilibration. The concentration of La(III) or Pr(III) were determined by atomic absorption spectroscopy method.

Adsorption capacity was calculated the following equation (1):

$$q = \frac{C_0 - C_t \cdot V}{m} \quad (1)$$

where: q is the adsorption capacity (mg/g or mmol/g) at equilibrium; C_0 andCt are the initial and equilibrium concentration of La(III), Pr(III) ion(mg/l), respectively; V is the volume (ml) of solution and m is the mass (g) of adsorbent used.

2.3.4. *Concentration of functional groups in PHA*

+ -COOH and -CONHOH groups:

The swollen PHA (0.2 g) was shaked with 50 ml of 0.25 M NaOH solution for 6 hours. When the reaction finished, the sample was filtered. The total filtrate was titrated with 0.25 M hydrochloric acid enough determination of the NaOH excess concentration. -COOH and -CONHOH group concentrations is calculated the following equation (2):

$$-\mathrm{COOH} + -\mathrm{CONHOH} = \frac{C_{NaOH}V_{NaOH} - C_{HCl}V_{HCl}}{m_0} \quad (2)$$

where: C_{HCl} is concentration of 0.25 M HCl solution; V_{HCl} (ml) is volume of 0.25 M HCl solution used; C_{NaOH} is concentration of 0.25 M NaOH solution; V_{NaOH} (ml) is volume of 0.25 M NaOH excess; m_0 is weight of PHA (g).

+ -COOH group:

The swollen of PHA hydrogel (0.4g) was shaked with 50 ml of 0.1 M $NaHCO_3$ solution for 12 hours, then the polymer was filtered and washed thoroughly with distilled water. The total filtrate was acidified with 50 ml 0.1 M HCl solution. -COOH group concentration is calculated the following equation (3):

$$-COOH = \frac{C_{NaHCO_3}V_{NaHCO_3} - C_{HCl}V_{HCl} + C_{NaOH}V_{NaOH}}{m_0} \quad (3)$$

where: C_{HCl} is concentration of 0.1 M HCl solution; V_{HCl} (ml) is volume of 0.1 M HCl solution used; C_{NaOH} is concentration of 0.1 M NaOH solution; V_{NaOH} (ml) is volume of 0.1 NaOH titrated; m_0 is weight of PHA (g).

3. RESULTS AND DISCUSSION

3.1. Effect of temperatures and reaction time to hydroxamic group contents

The modification process was performed pH= 14, 3.3 M $NH_2OH.HCl$ concentrations at various time and temperature. Effects of temperature and time to functional group contents in PHA acid) is showed in figure 1.

The figure 1 shows that when temperature increases from 25 to 30 °C, –CONHOH group contents increases and maximum –CONHOH group contents at 24 hours. When temperature increases from 40 °C to 50 °C, –CONHOH group contents decreases. Because when temperature increases, a part of –CONHOH groups hydrolyzed forming –COOH groups.

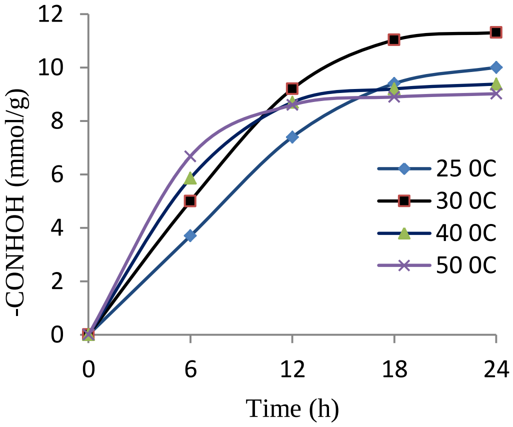


Figure 1: Effects of temperature and time to –CONHOH group contents

3.2. Effects of $NH_2OH.HCl$ concentrations, pH to functional group contents and characterization of poly(hydroxamic acid)

The modification process was carry out 30^{O}C, pH = 14, 24 hours, at various $NH_2OH.HCl$ concentrations. Effect of $NH_2OH.HCl$ concentrations tofunctional group contents in PHA is presented in table 1.

Table 1: Effect of $NH_2OH.HCl$ concentrations to functional group contents

$NH_2OH.HCl$ concentrations (M)	-COOH and -CONHOH (mmol/g)	-COOH (mmol/g)	-CONHOH (mmol/g)
1.0	9.94	1.45	8.49
2.0	10.93	1.57	9.36
3.0	12.23	1.61	10.62
3.3	13.02	1.68	11.34
3.5	13.06	1.72	11.34

The table1shows that $NH_2OH.HCl$ concentration has significantly affected the contents of functional groups in the PHA. When $NH_2OH.HCl$ concentrations increases, -CONHOH group contents increases.

Effects of pH to functional group concentrations of poly(hydroxamic acid) is presented in table 2.

The table 2 shows that pH has a strong influence to the contents of functional groups in the PHA. When pH from 11 to 12 modified process almost does not react (-CONHOH group contents is very small). At pH from 13 to 14, –CONHOH group content increases and maximum at pH=14. Therefore, modified process synthesize PHA need to perform at pH = 14.

The FTIR of PHA is shown in the figure 2. The FTIR spectrum of PAM showed the characteristic absorption band of amide (N-H), CH_2 stretching and carbonyl groups at 3369, 2926 and 1661 cm^{-1}. The FTIR spectrum of PHA resin (Fig. 3) showed the characteristic absorption bands of amide (N-H), carbonyl and (N-O) groups at 3436, 1668 and 1009 cm^{-1}.

The mechanism of the conversion of poly(acrylamide) to poly(hydroxamic acid) is shown in Scheme 2.

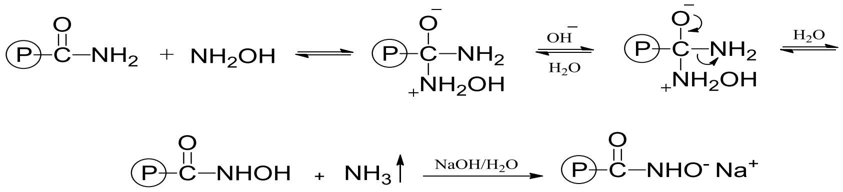
Scanning electron microscope (SEM) of PHA shown in figure 4. Monodispersed spherical particles from 50 to 120 nm in diameter were observed.

3.3. Study on adsorption of La(III), Pr(III) ions by poly(hydroxamic acid)

The adsorption of La(III), Pr(III) ions on poly(hydroxamic acid) take place under Langmuir adsorption isotherm model.

Table 2: Effect of pH to functional group contents

pH	-COOH and -CONHOH (mmol/g)	-COOH (mmol/g)	-CONHOH (mmol/g)
11	2.75	1.50	1.25
12	3.78	1.75	2.03
13	7.38	1.70	5.68
14	13.02	1.68	11.34



Scheme 2: Reaction mechanism of converting poly(acrylamide) into poly(hydroxamic acid) via treatment with hydroxylamine in an alkaline medium
where: P - polymer backbone

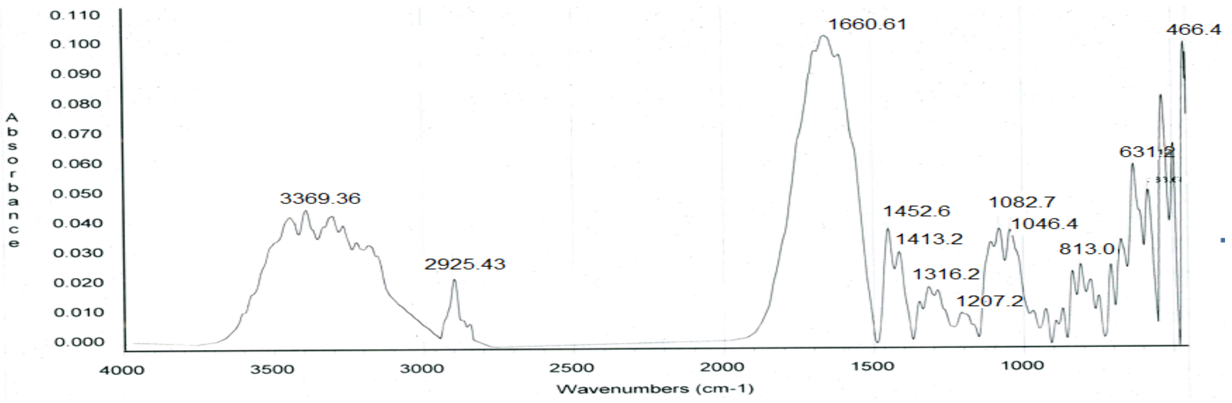


Figure 2: FTIR spectra of polyacrylamide

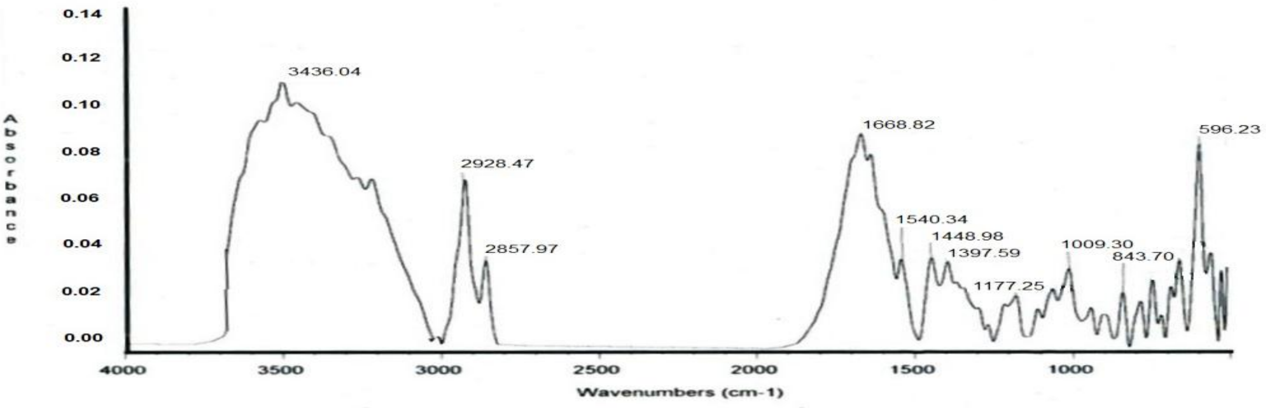


Figure 3: FTIR spectra of poly(hydroxamic acid)

The Langmuir isotherms were constructed from the results obtained in adsorption process of La(III), Pr(III) ions following equation (4):

$$q = q_{max} \cdot \frac{bC_t}{1+bC_t} \qquad (4)$$

where: q is the adsorption capacity at equilibrium, q_{max} is the maximum adsorption capacity and b is constants.

To determine b constants in the Langmuir isotherm equation can transfer that equation in the linear equations (5):

$$\frac{C_t}{q} = \frac{1}{q_{max}} \times C_t + \frac{1}{b.q_{max}} \quad (5)$$

This is the curvature of the equation depends Ct/q on Ct. From this linear equations might determine Q_{max} and b constants in the equation from the axis of the slope and cut seats.

Based on the optimal conditions was conducted adsorption process La(III) and Pr(III) ions with different concentrations. The adsorption data were analyzed according to the Langmuir adsorption isotherm model. Linear form of Langmuir adsorption isotherm is shown in the figure 5.

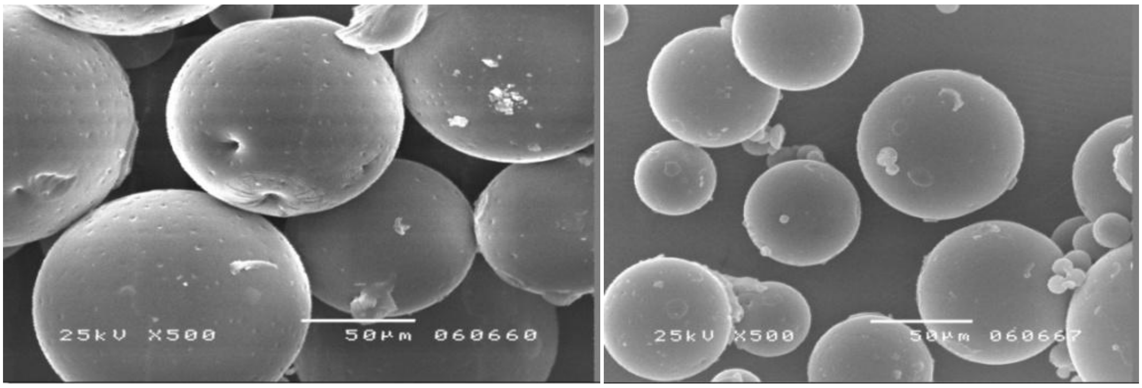
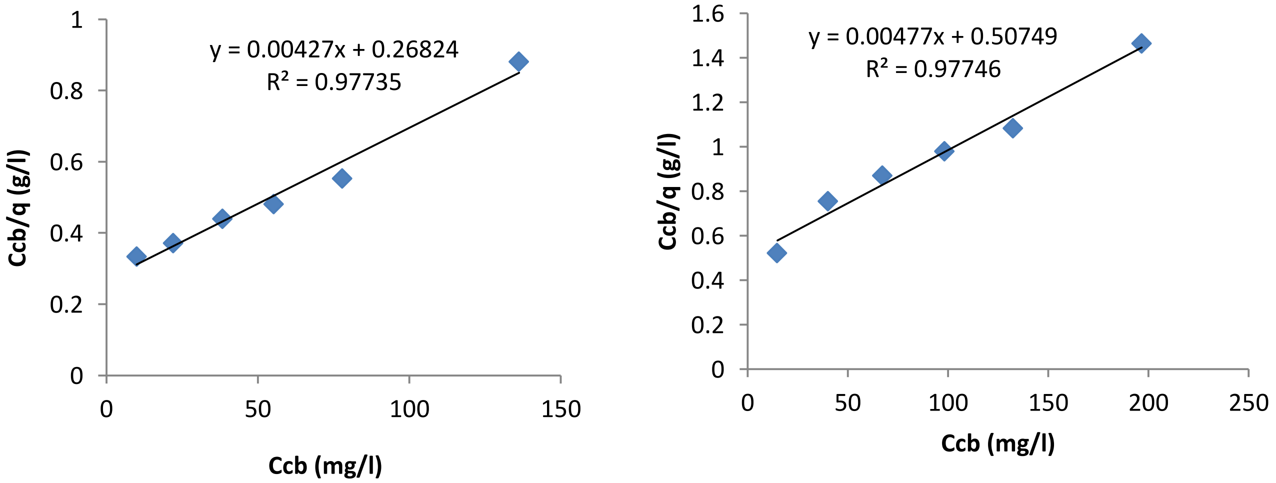


Figure 4: SEM images of poly(hydroxamic acid)



a) b)

Figure 5: The linear form of the Langmuir adsorption isotherm for a) La(III) and b) Pr(III)

As can be seen that linear form of Langmuir adsorption isotherm describe exactly the adsorption process of La(III) and Pr(III) ions by poly(hydroxamic acid). The maximum adsorption capacity of La(III) and Pr(III) ions (q_{max}) was 209.64 and 234.19 mg/g, repectively and b constants of La(III) was 0.26824 and Pr(III) was 0.50749.

4. CONCLUSION

Studied on synthesis poly(hydroxamic acid) by modification process of polyacrylamide with hydroxylamine hydrochloride under optimal conditions: 30 ^{o}C temperature; 24 hour, 3.3 M $NH_2OH.HCl$ concentrations and pH = 14. Characterization of poly(hydroxamic acid) were studied by FTIR and SEM.

The adsorption of La(III) and Pr(III) ions by poly(hydroxamic acid) conformed to linear form of Langmuir adsorption isotherm. Adsorption capacity for La(III) and Pr(III) were found as 234.19 and 209.64 mg/g, respectively.

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