Synthesis, Characterization of P(CH/AA-co-AM) and Adsorptive Removal of Pb (II) ions from Aqueous Solution: Thermodynamic Study

Aseel M Aljeboree[1*], Rasha Amer Mohammed[2], Makarim A. Mahdi[3], Layth S. Jasim[4], Ayad F. Alkaim[5]

Abstract

Cross-linking Chitosan/Poly (Acryl amide-Acrylic acid) Hydrogel (P(CH/AA-co-AM)) synthesized via free radical polymerization of Acrylamide and acrylic acid as monomers after that addition chitosan, using MBA and KPS as initiator. The produced materials' structural, surface, and thermal properties were determined using the following techniques: FT-IR, TGA, TEM, and FE-SEM. This study is concerned with a significant application of surface chemistry in the fields of removing heavy metals. It deals with the adsorption-systems of Pb (II) on Cross-linking Chitosan / Poly (Acrylic acid-Acryl amide) Hydrogel at variable conditions of concentration and temp. The measured data are following the Freundlich equation and, according to the Giles classification, the adsorption isotherms are of type S3. As a temperature feature (10, 20, 25 and 30oC), adsorption was investigated. With increasing temperature (endothermic process), the extent of adsorption of Pb (II)on P(CH / AA-co-AM) was found for increase. They have also measured the essential thermodynamic functions.

Key Words: Adsorption, Removal, Hydrogels, Pb (II), Isotherms, Thermodynamic.

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Introduction

A thorough examination of the toxicity of heavy metals to plants and animals has been conducted. Since this weighty metal isn't bio-degradable, they head for compile in the living organism, resulting in a variety of diseases and ailments. Hydrogels, for example, can be used to remove heavy metal ions from a polluted aquatic system (Ricordel 2001; Ruwaida A Raheem 2016; Uddin 2017). Due to the significantly reduced cost of the bulk material, hydrogels offer enormous promise for usage in the removal of a variety of metals from aqueous solutions. A hydrogel is a three-dimensional network of polymers that can expand in the presence of water as a result of the physical or chemical cross-linking of individual polymer chains. Hydrogels also exhibit some flexibility as a result of their high water content. The hydrophilicity of the hydrogel is a result of the existence of hydrophilic groups such as $-SO_3H$,$-NH_2$,-OH,-COOH, and-CONH and-$CONH_2$. (Jasim, Radhy et al. 2015; Al-Hayder and Al-Hussainawy 2016).

Corresponding author: Aseel M Aljeboree

Address: [1*]Department of Chemistry, College of Sciences for Girls, University of Babylon, Hilla, Iraq; [2]Department of Chemistry, College of Education, University of Al-Qadisiyah, Diwaniya, Iraq; [3]Department of Chemistry, College of Education, University of Al-Qadisiyah, Diwaniya, Iraq; [4]Department of Chemistry, College of Education, University of Al-Qadisiyah, Diwaniya, Iraq; [5]Department of Chemistry, College of Sciences for Girls, University of Babylon, Hilla, Iraq.

[5]E-mail: annenayad@gmail.com

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Adsorption is a significant surface phenomenon that often refers to the concentration of a particular component at an interface with another solution or bulk phase (Akhtar, Amin et al. 2015). Adsorption may also be described as the accumulation of ions, atoms, or molecules on a surface (Yu, Peldszus et al. 2008; Alyaa Kareem 2016; Ayad F. Alkaim 2016; Aljeboree 2019). Charcoal was the most solid surface used physically to cleanse wastewater containing polluting heavy metals (M. Ghaedi 2011; Mona Karnib 2014). Other active surface materials besides charcoal have been researched and found to be capable of removing chemical pollutants from water, such as The expense, on the other hand, is significant, and retrieving activated carbon particles from treated water may be challenging (Aljeboree 2019; Zhang 2019; Mohib Ullah 2020). Hydrogel resources could be used to treat hazardous waste (such as heavy metals, dyes, and phenols) at a lower cost. Polyacrylamide, GO/Poly Acrylic Acid–Maleic Acid, GO/Polyvinylpyrrolidone–acrylic acid, HPMC-co-AA, and CMC-g-polyacrylamide have all been utilized for this purpose (Malik, Jain et al. 2016). The purpose of this work is to determine the adsorption capacity of Hydrogel for lead ions in aqueous solution under various concentration and temperature circumstances and to compute the thermodynamic parameters under these settings.

Experimental

Materials and Chemicals

Acrylic acid, Acryl-amide, acetic acid, and TEMED were supplied by (Himidia, India), the initiator KPS (potassium-persulfate) has been supplied by (Fluka, German). We purchased N, N'-methylene bisacrylamide, a multifunctional crosslinker (Fluka, Germany). organic compounds and were supplied by inorganic compounds (Merck, Germany).

P(CH/AA-co-AM) Preparation

Add 6g of acrylic acid (AAc) to Sodium Hydroxide to make the initial solution. Following that, it is necessary to dissolve and mix Acrylamide (AAm) (6g in 10ml D.W) with MBA (0.05 gm. in 5 ml D.W). For 15 minutes, the solute was kept in the stirrer. 2nd Alternative Prepare by stirring 1g of chitosan in 2% CH_3COOH for 15minutes at 60cC. Following that, K.P.S (0.1 g in 5 mL D.W) is combined with TEMED (0.05 g in 5 mL D.W). The first solution was added drop by drop to the second solution at a temperature of 60oC. Allow it to soak in bathwater for two hours to form the P(CH/AA-co-AM) hydrogel. The hydrogel powder was rinsed extensively with distilled water, numerous times, to remove nearly all soluble components. After washing the hydrogel, it was dried in an oven at 60oC for 3 hours and stored in airtight containers. This hydrogel was then used in all of the experiments in this work.

Calibration Curves

Serial dilutions were used to prepare solutions of various concentrations of Pb (II). The absorbance values of these solutions at the selected maximum value were determined using an atomic absorption spectrophotometer (FAAS, Shimadzu, AA-6300) and plotted against the conc. value (Figure (1)). We used calibration curves in the conc. the range covered by Beer-law. Lambert's.

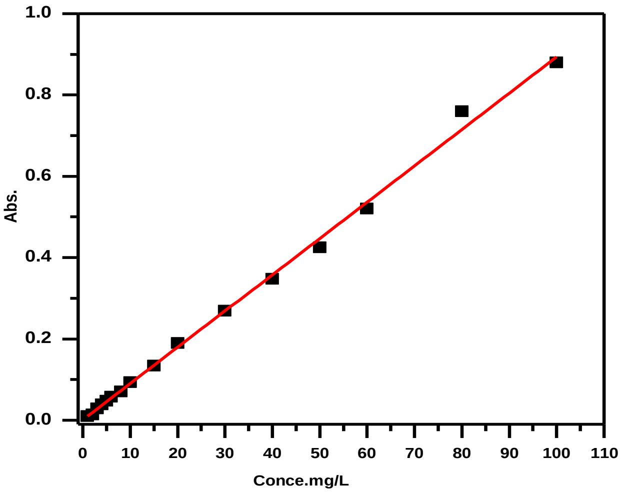

Figure 1. Calibration curves of Pb (II) ions

Adsorption Isotherm

Each solution (10 mL) was added to the flask with 0.05g of hydro-gel at known doses (10 - 800 mg/L). The flasks were shaken at a rate of 60 cycles per minute in a thermostatically controlled water bath until equilibrium was achieved. The centrifugation duration was either 20 minutes at 3000 rpm or 20 minutes at 1000 rpm. Calibration curves were used to determine the equilibrium concentrations. This equation helped measure the amount of medication absorbed. (Zaied A. Mosaa 2019):

$$Q \text{ or } \frac{x}{m} = \frac{V(C_o - C_e)}{m} \qquad (1)$$

Where:

x is the quantity adsorbed, m is adsorbent weight (g), C_o is initial-concentration (mg/L), C_e is

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equilibrium-concentration (mg/ L) and V is solution volume (L).

Results and Discussion

Characterization

To conduct a preliminary qualitative investigation of the principal functional groups present on hydrogel surfaces, FTIR spectroscopy was used. (Figure (2)).

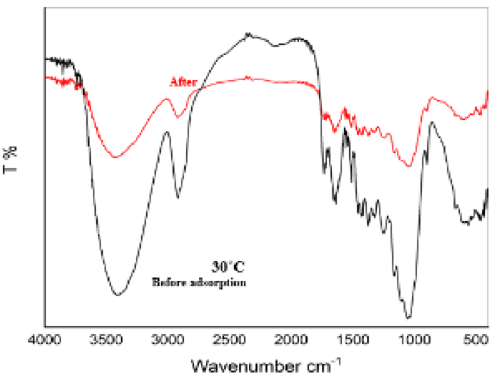

Figure 2. FTIR-spectra of Hydrogel before and after adsorption of Pb (II) ions

The FTIR spectra of Pb (II)) - loaded adsorbent Hydrogel was obtained and Figures (2). As compared to FTIR spectra of the Hydrogel surface, the decrease in intensities of broad absorption bands at 3300 and 3450 cm^{-1} Hydrogel was observed. The shift in the intensity of bands corresponding to the amino and hydroxyl groups in the FTIR spectrum suggested that these two groups may be involved in metal sorption. Biosorption and ion exchange occur together. Heavy metal ions were used to replace hydrogen ions in carboxyl, hydroxyl, and amino groups (Layth S. Jasim 2021).

FE-SEM was used to investigate the morphologies of Hydrogel before adsorption. (Figure (3)) illustrates the FE-SEM investigation of Hydrogel's tendency to aggregate into multilayer agglomerates. Following adsorption, the hydrogel becomes roughened and the Pb (II) ions are uniformly dispersed as brilliant spots across the hydrogel. These findings establish the presence of Hydrogel and Pb (II) ions (Salam H. Alwan Altaa 2018).

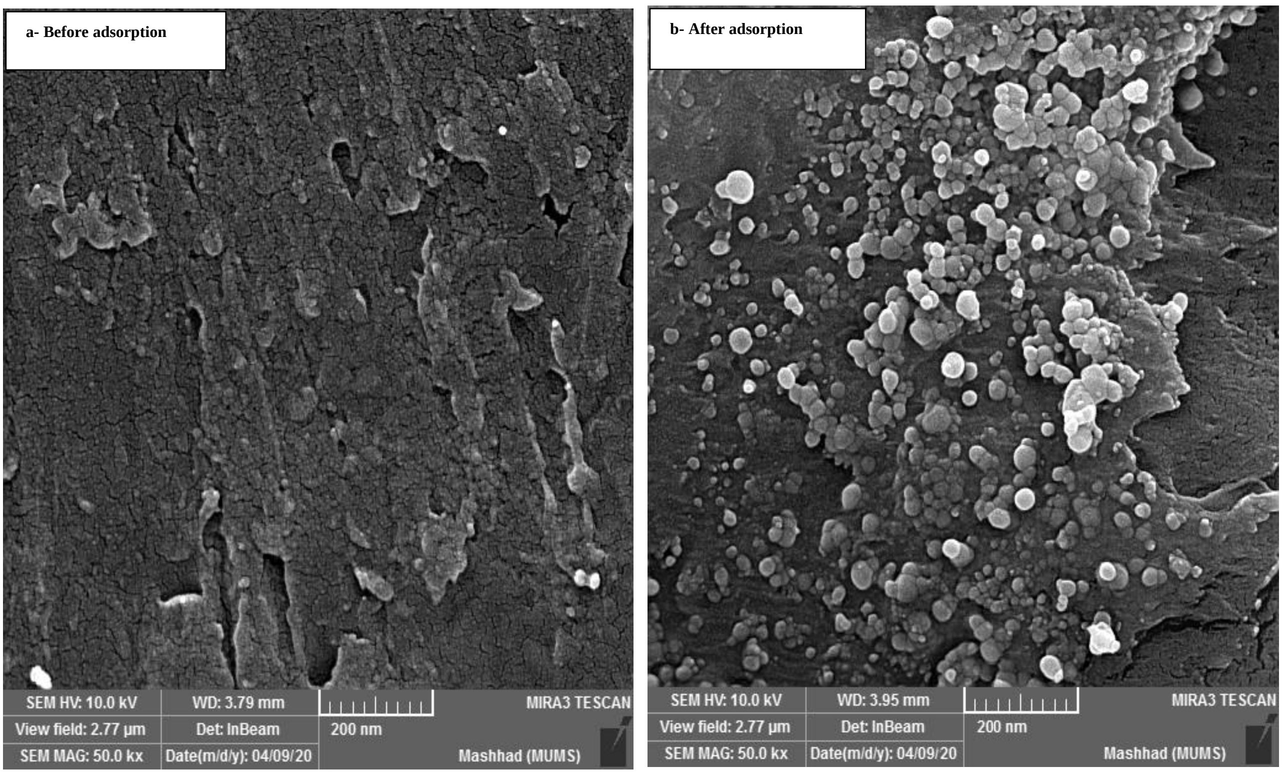

Figure 3. FE-SEM analysis of Hydrogel: a- before, b-after adsorption

Thermo gravimetric Analysis (TGA) methodology was used to heat the samples (40- 900) °C at a rate of 10°C min^{-1} under N_2 environment. TGA spectroscopy The hydrogel in Figure (4) exhibits no weight loss up to 180°C, indicating the hydrogel's exceptional thermal resilience (Basam W. Mahde 2018).

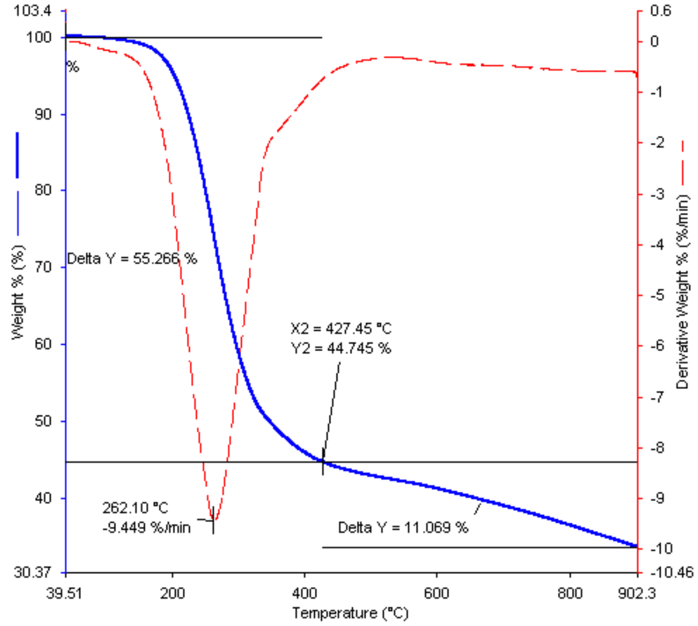

Figure 4. TGA analysis of Hydrogel

Morphology of Hydrogel before and after adsorption was assessed by TEM (Figure (5)). Hydrogel appears translucent, homogenous, silky, and stable when exposed to a high-energy electron beam in the TEM image (Layth S. Jasim 2018; Rashi Gusain 2019). In this step, the bonding between the layers cannot demolish. For this reason, the hydrogel moving towards interlacement with each other in a regular way and yield multiple-layer agglomerates. Hydrogels work on the good associate on of adjacent Pb (II) particles.

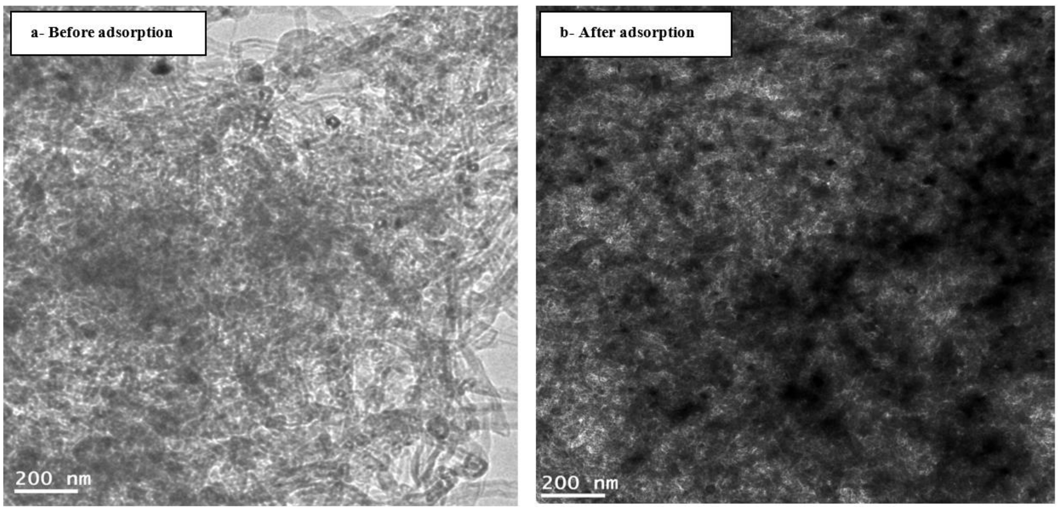

Figure 5. Transmission electron microscopy images of P(CH/AA-co-AM): a- Before adsorption, b- After adsorption

Adsorption Isotherm Models

At constant temperature, the adsorption isotherm represents the relationship between the amount of substance adsorbed and the residual concentration of the adsorbate in the solution (J. Chatterjee 2014; Tian 2019). The Langmuir, Freundlich, and Temkin isotherms were used to test the adsorption equilibrium data. A linear relation is usually used to define the suitable isotherm and the applicability of isotherm equations according to the correlation coefficients. Freundlich isotherm represents the linear relationship between log C_e versus log C_e. Figure (6) and Table (1) show that Pb (II) ions apply to this isotherm depending on the correlation coefficient. This indicates that the surface is heterogeneous and multi-layer adsorption with a difference in energy between active adsorption sites.

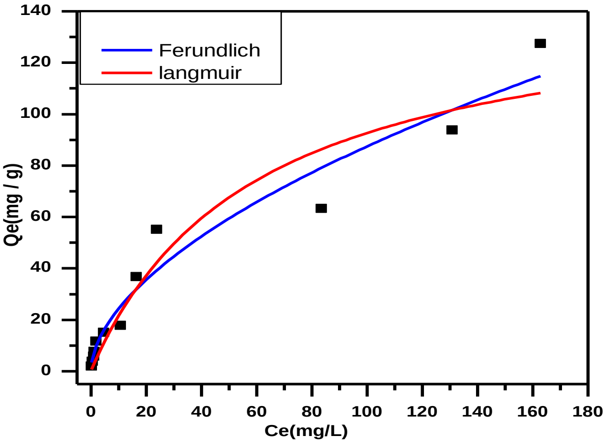

Figure 6. Freundlich and Langmuir isotherms of metal ions on Hydrogel

Table 1. Langmuir, Freundlich and Temkin isotherm constants for metal ions uptake by Hydrogel

	Langmuir equation			Freundlich eq.		
	K_L (L/mg)	q_m (mg/g)	R^2	K_F	n	R^2
Pb (II)	0.069	73.529	0.8628	4689	0.089	0.9700

Adsorption of Pb (II) at Different Temperature

The adsorption of Pb (II) ions from aqueous solution on poly (CH/AA-co-AM) has been studied at 25°C and other three temperatures (10, 20, and 30°C) Figure (7).

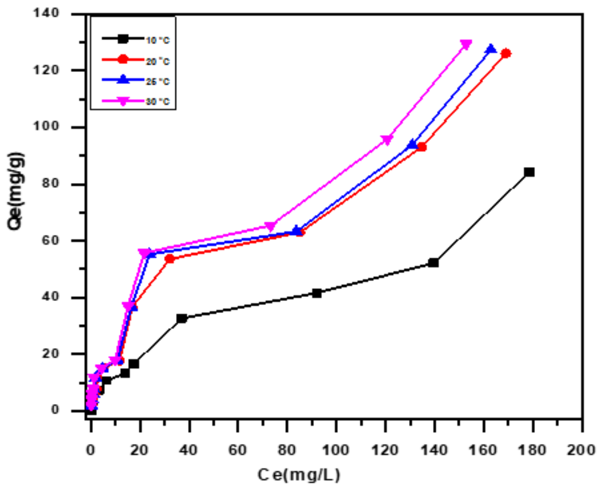

Figure 7. Effect of temperature on adsorption of Pb (II) on Hydrogel)

The basic thermodynamic quantities of adsorption of Pb (II) ions on Hydrogel were estimated by calculating X_m values at different temperatures (Table (2) and Figure (8)) demonstrate these calculations.

Table 2. The effect of temperature on the highest quantity adsorbed of Pb (II) ions on the hydrogel surface

$T^{o}{}_{C}$	T_K	$1000 / T_K$	Ce = 153 mg/L	
			X_m (mg/g)	ln X_m
10	283	3.534	61	4.110
20	293	3.413	109	4.691
25	298	3.356	116	4.753
30	303	3.300	129	4.859

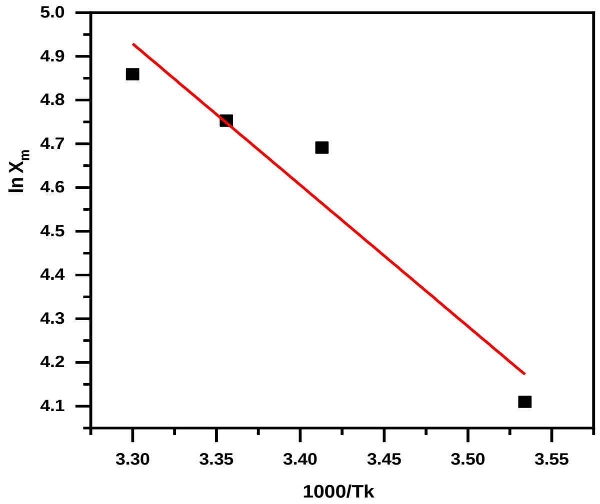

Figure 8. Plot of ln Xm against reciprocal absolute temperature for adsorption of Pb (II) ions on Hydrogel

The thermodynamic amounts of Pb (II) ions have been determined Endothermic heat of adsorption is displayed when a hydrogel system is being used, whereas entropy is positive in Table (3). The aforementioned phenomenon can be understood by reference to the hydrophobic binding of water molecules that had formerly surrounded both Pb (II) ions and the active sites. The current disruption of the hydrophobic bonding with the orderly iceberg structure of water molecules previously surrounding both Pb (II) ions and the active sites leads to an increase in randomness (P. Xu 2012; M. Chiban 2016). although the negative ΔG values imply that the system spontaneously undergoes a process and because the system does not derive energy from an external source.

Table 3. Values of thermodynamic functions of the adsorption process of Pb (II) ions on Hydrogel at 25°C

Equilibrium Constant (K)	**ΔS** (J.mol^{-1}.K^{-1})	**ΔG** (kJ.mol^{-1})	**ΔH** (kJ.mol^{-1})
15.163	112.591	-6.623	26.929

Conclusions

In this study, P(CH/AA-co-AM) hydrogel was prepared, identification and used as an effective absorbent for removing Pb (II) ions from aqueous solution. The Pb (II) ions adsorption follows the Freundlich isotherms. Due to the higher activity of hydrogel surface in adsorption of the pollutants, they can be used for the elimination of Pb (II) ions from water or waste water. Thermodynamic parameters for the removal of Pb (II) are computed and it is discovered that the amount of heavy metal ions adsorbate rises with increasing temperature, indicating that the process is spontaneous and endothermic.

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