Adsorption and removal studies of heavy metal Pb(II) on their Water Solution on adsorbent surface of Vinyl Alcohol/Chitosan-Graphene Oxide

Layth S. Jasim*1 and Sajjad H. Irhayyim2

1,2Department of Chemistry, College of Education, University of Al-Qadisiyah, Diwaniya, Iraq
layth.alhayder@qu.edu.iq

Abstract
Chitosan / polyvinyl alcohol/graphene oxide (CH-g-PVA/GO) hydrogel was prepared by using iron chloride as a cross-linking agent. This hydrogel was used to remove lead ions as it was found to have a suitable surface area for adsorption time was 120 mint. The adsorption is proven using FESEM and FTIR analysis, TEM analysis, and knowledge of AFM surface roughness. Also, TGA shows that the hydrogel is stable at high temperatures. The study of the hydrogel's kinetic parameter was performed by using the lead ion applied to the adsorption of the pseudo-second-order because (R^2) approximates the correct model.

Keywords: Adsorption, Heavy elements (Pb(II)), Graphene oxide, polyvinyl alcohol, Hydrogels.

Introduction
Water pollution with heavy metals is a global environmental problem due to the significant increase in the levels of heavy elements in water [1]. Through the continuous development and the large increase in the population and factories, we note that human activities significantly impact water pollution with heavy metals, such as wastewater drainage and liquid waste disposal from industries, especially in densely populated areas and industrial areas [2-4]. Contamination of water with heavy metals leads to a change in water properties, such as taste, color, odor, turbidity, and pH [5], even in low concentrations, can be very injurious to humans [6]; Heavy metals are among the most serious environmental problems due to their biological toxicity, Difficulty with breakdown, long half-life and ability to enter the food chain [7]. Heavy metals such as lead are toxic metals that, when consumed above the permissible level can lead to chronic diseases such as high blood pressure, kidney and liver problems and skin irritation, is a mineral with a relatively low concentration, which is insoluble and highly toxic to humans and living organisms [8,9].
Removing toxic heavy metals from water is of great importance in providing necessary health and environmental protection. One method used is the adsorption of hydrogels [10]. One of the materials applied to remove pollutants and impurities from water and their modified derivatives was graphene oxide, which can absorb suspended and water-soluble materials due to its large surface area [11]. Graphene oxide used to remove lead from water, it found to be a good material for absorbing lead due to the functional groups (hydroxyl, carboxylate) that is, the high concentration of negatively charged groups on the surface, which results in the attraction of many pollutants, including heavy metal ions (positively charged), as it provides a suitable porous structure to absorb toxic metals efficiently [12, 13]. The present research aims to explore the feasibility of using cross-linked hydrogels (CH-g-PVA/GO) and study of the adsorption of heavy elements (Pb(II)) from their aqueous solution on the surface of the hydrogel superimposed chitosan, polyvinyl alcohol, graphene oxide.

**Experimental**

**Chemicals and materials**

Chitosan was supplied (Himedia, India). (Sigma-Aldrich, Germany) supplied Graphene Oxide (GO). (Merck, Germany) supplied polyvinyl alcohol (PVA). (Fluka, Germany) supplied iron chloride (FeCl3). (Merck, Germany) supplied iron sulfate (FeSO4). Lead nitrate (Pb(NO3)2) was supplied by (Alpha Chemika). (Merck, Germany) supplied acetic acid (CH3COOH). (Merck, Germany) supplied sodium hydroxide (NaOH).

**Preparation of (CH-g-PVA/GO) hydrogel**

To prepare hydrogel (CH-g-PVA/GO) we dissolve (4g) of chitosan in (100ml) of acetic acid at a concentration of (3%), then stir with the motor, At a temperature of 60 °C for (60) minutes, then prepare a solution of (PVA) by dissolving (4g) of it in (100ml) of distilled water and at a temperature of 80 °C with constant stirring for (6) hours, after that we prepare a solution of (GO) Dissolving 0.05g of it in 100ml of distilled water and then placing it in the ultrasound machine for one hour. Then we prepare the crosslinking agent (FeCl3), iron chloride (3.24g) and dissolve it with a small amount of water. We prepare iron sulfate (FeSO4) by taking a quantity of (1.5g) from it and dissolving it with a small amount of water. After that, we mix the solutions by adding the chitosan solution to the PVA solution with continuous stirring and at a temperature of 70 °C for a period of (30) minutes. We add the (GO) solution to the formed solution and also with continuous stirring for (15) minutes, followed by adding Crosslinking agents (FeCl3) and (FeSO4) slowly with continuous stirring for (60) minutes. Then we prepare (500ml) of (NaOH) (10% w / v). We distill the resulting solution in the form of drops using a syringe and then leave the product for a period of (5) hours. We wash the material formed with distilled water without ions until reaching pH = 7. We dry it at a
temperature of 60°C for a period of (24) hours, after which it is left at 40°C for a period of (24) hours, and then ground to obtain a constant weight of the compound hydrogel.

**Adsorption Isotherm**

Different concentrations of zinc Lead ion solution ranging from (10-100) mg/L were prepared by placing 0.05 g of aqueous gel (the adsorbent surface) in 10 ml of each concentration. These concentrations were placed in a shaker for 120 minutes. The filter absorption calculated after separating it from the centrifuge for 15 minutes at 6000 revolutions per minute using a (UV-Vis spectrum) device, and the concentrations calculated according to the following law:

\[ Q_e = \frac{(C_o-C_t) \cdot V_{ml}}{m} \]  

(1)

The percentage of adsorbent removal can be determined through the following equations:

\[ Re \% = \frac{(C_o-C_t)}{C_o} \times 100 \]  

(2)

Where Qe represents the amount of adsorbed material, Co and Ct are the initial and equilibrium concentrations for the adsorbent the solution in mg/L, respectively; m is the hydrogel mass in mg. V is the volume of the solution in L [14-15].

**Results and Discussion**

**Characterization**

The analysis was done by FT-IR for CH-g-PVA/GO (Figure (1)) below. At (3400-3525 cm\(^{-1}\)) shows hydroxyl group interfering with the amine group package (3415 cm\(^{-1}\)) Indicates the presence of graphene oxide in the compound, and the beam that appears at (1650 cm\(^{-1}\)) confirms the presence of the associated alkyl groups and that the beam is at (1400-1550 cm\(^{-1}\)) It refers to the carbonyl group With the presence of graphene oxide, this indicates the hydrogen interaction between the graphene oxide sheets and the polymeric chains., but at (1357 cm\(^{-1}\)) it refers to the carbonyl group in the carboxyl group and the bundle (1319 cm\(^{-1}\)) refers to the bond between nitrogen and carbon. Band (1061 cm\(^{-1}\)) refers to iron chloride. After adsorption, the adsorption beams of the active groups present on the compound's surface are shifted and decreased due to the hydrogen bonding with these groups [14, 15].
Fig. 1: FT-IR analysis for CH-g-PVA/GO Before and after Lead ion (Pb(II)) Adsorption

The analysis by technique FE-SEM that Hydrogel Poly (CH-g-PVA/GO)) micrographs of hydrogels demonstrate that they have porous structures Figure (2). That is, they have good sites of absorption and structure of composite membranes with shell-like shape. The pores are interconnected. This is due to the strong bonding of the polymeric chains by the cross-linking agent and enhances the hydrogel's swelling rate. After adsorption, the surface images appear. The appearance becomes rough due to the grafting with Lead ion (Pb(II)) due to the filling of the pores and the interconnection of the adsorbed Lead ion (Pb(II)) molecules with the active centers of the adsorption surface, and the Lead ion (Pb(II)) particles are visible on the surface of the compound; this indicates that the adsorption process has occurred [16, 17].

Figure (2): FE SEM

TEM analysis of hydrogel poly (CH-g-PVA/GO) has small granules and uniform distribution. It has excellent dispersion, uniformly arranged, and lumpy, which belongs to the chitosan matrix. After adsorption, the poly (CH-g-PVA/GO) is covered with heterocyclic nanoparticles of Lead ion particles Figure (3) [18].
The thermal behavior (TGA) of the CH-g-PVA/GO compound has been studied by TGA, which measures the change in the sample mass within the thermal range (0-900) °C with a heating rate of 100°C / min in the presence of gas. Nitrogen, Figure (4) and Table (1) shows that the prepared hydrogel compound is very stable within the temperature range of (0-25)°C and does not suffer breakage at this temperature range and when the temperature reaches the range of (25 -244°C) begins with a slight dissolution of 3.90 and is attributed To water molecules adsorbed on the surface, and when the temperature range reaches (244-332)°C part of it is dissolved by (23.51%) in the form of CO₂, CO, which is due to the removal of the host groups containing the oxygen atom such as COOH, OH, and COC(9). The temperature range is between (332-548), the decomposition in it is at (17.1%), which is attributed to the thermal breakdown of the interlocking polymeric chains of the hydrogel complex, The temperature range is between (548-743)°C, the decomposition in it is at(10.8) [19].

![Fig. 3: TEM for (CH-g-PVA/GO) after and before adsorption](image1)

![Fig. 4: The carve of stability for (CH-g-PVA/GO) by using TGA](image2)
Table 1. Thermal decomposition values CH-g-PVA/GO

| Stage | TGA Range(°C) | Mass Loss | DTA(°C) |
|-------|---------------|-----------|---------|
| 1     | 25-244        | 3.90      | 212(+)  |
| 2     | 244-332       | 23.51     | 303(+)  |
| 3     | 332-548       | 17.1      | 598(-)  |
| 4     | 548-743       | 10.8      | 737(-)  |

Using atomic force microscopy, the prepared surface's external shape analyzed, which gives a three-dimensional image of the sample's shape through which statistical information can obtain on the surface roughness values of the surface roughness (Figure (5) and Table (2)) [20].

Table 2. Statistical roughness coefficients for CH-g-PVA/GO

| H-g-PVA/GO | The statistical value of roughness          |
|------------|--------------------------------------------|
| 2.373      | Roughness rate($R_a$)nm                     |
| 3.399      | Average square root of roughness($R_q$)nm   |
| -1.631     | Torsion of the surface($R_s$)nm             |
| 10.04      | Flat peaks($R_{pk}$)nm                      |
| 11.08      | The upper limit of the height of the peaks($R_p$)nm |
| 20.57      | Minimum roughness depth($R_v$)nm            |
| 31.66      | The maximum height of the rough surface($R_z$)nm |

Figure 5: 3D image of the atomic force microscope (CH-g-PVA/GO)
Adsorption Kinetics Study and Equilibrium Time Effect

Through practical experiments, the kinetic models of lead ion absorption were accurately determined on the Chitosan-PVA / GO union's surface and the percentage removal of Pb(II) shown in Figure (6).

![Figure 6. Effect of reaction time on Lead ion adsorption.](image)

By analyzing the two pseudo-pseudo-models of the first and second-order Figure (7). Where the kinetic constants and correlation coefficients were calculated for the adsorption process as in Table (3), where it was noticed that the value (R2) of the second-order false model is much higher than the first false model, so the adsorption of the lead ion solution is considered a first-order error [21-23].

![Figure 7. Effect of reaction time (A), pseudo-first-order (B), and the pseudo-second-order (C) on Lead ion adsorption.](image)
Table 3. Kinetic adsorption coefficients of Lead ion on (CH-g-PVA/GO)

|               | Slope (g. mg⁻¹.min⁻¹) | Intercept | Slope |
|---------------|-----------------------|-----------|--------|
| Pseudo-first order Pb(II) |                       |           |        |
| R²            | qₑ (mg/g)             | kₚ(min⁻¹) |        |
| 0.7374        | 16.22414              | 0.0032    | 2.7865 |
|               |                       |           | -0.0032|
| Pseudo-second order Pb(II) |                   |           |        |
| qₑ (mg/g)     |                       | kₑ (mg⁻¹.min⁻¹) |       |
| 0.1067        | 0.132846              | 8.57      | 0.1067 |

Conclusion

A study of the CH-g-PVA/GO performed using lead ion. Due to the compound's high absorption activity, it can be used to absorb lead ions. The results showed that the compound had an increased ability to absorb lead ions through the results of (SEM-TEM) and absorption from the pseudo-second-order model (R² = 0.9997) (A pseudo-second-class comparative model).

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