Kinetic Study of removal Zinc Oxide Nanoparticles from Aqueous Solutions on synthesized CH-g-P(AAc-co-Am)

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Abstract
The research contains the preparation of Cross-linking Hydrogel (Chitosan-g-poly (AA – Co – Am)). The way polymerization of the free radicals via utilizing the potassium persulfate as the initiator for the reaction, too with N, N'-methylene bis-acrylamide (NMBA)as a cross-linking agent The mixture gets treated via Acrylamide that includes The adsorption time was 120 mint. The adsorption was proved via utilizing the FESEM and FTIR analysis and analysis TEM And knowing the surface roughness AFM. Also, TGA appears that the hydrogel is stable at high temperatures. The kinetics parameter Study of the Hydrogel was performed via utilizing the Zinc oxide applies to the adsorption from the Pseudo-second order model Because (R²) an approximation of the correct one.

Keywords: Adsorption, Zinc oxide nanoparticles, Chitosan, hydrogel, kinetic, Equilibrium.

1.Introduction
Pollution is the most widespread major problem that has caused a defect in the ecosystem and a dangerous problem that threatens human life. Therefore, it isn't easy to obtain clean water in the existence of large amounts of wastewater. In all industrial countries, the ratio of water pollution that affects the human system is increased[1-4].

Toxins in wastewater can be removed using an adsorption process. Especially it is acceptable if the goal pollutant is non-degradable, as in the case of heavy metals, so the technology of destruction isn't successful [5]. Adsorption can also be economically profitable instead of finding adsorbents that optimize other technologies, to Per unit adsorbent mass, the removal of pollutants [6, 7]. In this case, the adsorbing substance displays a beneficial adsorption activity, that is, slightly greater than the residual level in the wastewater, the amount of the pollutant on its surface at equilibrium. Therefore, if such a condition is satisfied, it indicates that the counter-process, i.e. desorption, is adverse[8]. The adsorbents' inadequate or slow desorption regeneration can be a severe problem [9]. The aim of the present research is to explore the feasibility of using cross-linked hydrogels (Chitosan-g-Poly)(AA-co-Am) as a bacterial adsorbent. To examine the mechanism of bacterial adsorption and optimization of different parameters in bacterial recovery, equilibrium and kinetic analysis were performed.

2.Experimental
Chemicals and materials
Acryl amide ware supplied by (Himedia, India). The initiator potassium persulfate (KPS) was supplied by (Merck, Germany). The multifunctional crosslinker is N,N'-methylene bisacrylamide (NMBA) was purchase from (Fluka, Germany). Sodium chloride was obtained from (Alpha Chemika). Zinc oxide was purchase from (Sigma-Aldrich, Germany).
Preparation of poly (CH-(AAc-CO-Am))
To prepare hydrogel (CH/AA-CO-AM)) we prepare two solutions as following: Prepare the hydrogel compound (Chitosan-g-poly (AA – co – Am)) from a group of solutions starting from the preparation of a concentration of (% v / v1) of AA, as well as (0.5 g) of chitosan was dissolved in (30 ml) of AA, and stirred by Magnetic stirrer (hot plate) stirrer for 60 minutes at a temperature of 40°C. then prepare a solution of potassium persulfate Kps dissolving (g0.1) of it in 2ml of water, and preparing a solution of acryl amide (AM) by dissolving (2g) of it in (2ml) of water, as well as preparing a binder solution from MBA (N, N - Methylene - Bisacrylamide) by dissolving (0.05g) of it in (2ml) of water, then adding the initiater solution KPS in drops to the Chitosan solution with stirring, then adding the AM solution with continuous stirring for a period of 5 min, and added MBA cross-linking agent to solution with stirring and add N2 gas for 5 min, and then the solution is placed in the water bath at 50°C for 2h to complete the reaction, then the polymer is taken and washed with distilled water and dried in an electric oven at a temperature 60 °C [10-12].

Scheme 1. The formation of Hydrogel equation

Adsorption Isotherm
Prepare Different concentrations of zinc oxide solution ranging from (10-100) mg / L were prepared by placing 0.05g of aqueous gel (the adsorbent surface) in 10ml of each concentration. These concentrations were placed in the shaker for 120 min. The absorbance of filtrate was calculated after Separating it to the centrifuge for 15 min at a speed of 6000 rpm using a (UV-Vis spectrum) device, and the concentrations were calculated according to the following law[13]:

\[
Q_e = \frac{(C_0-C_t)V_{tot}}{m}
\]

(1)

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

**Adsorption % = \frac{(C_0-C_t)}{C_0} \times 100**

(2)

Where \( Q_e \) represents the amount of adsorbed material, \( C_0 \) and \( C_t \) are the initial and equilibrium concentrations for the adsorbent the solution in mg/L, respectively, \( m \) is the mass of hydrogel in mg. \( V \) is the volume in L.
3. Results and Discussion

Characterization

FTIR analyzed CH-g-poly(AAc-CO-Am)) show in Figure (1), at (3300 cm\(^{-1}\)) shows hydroxyl group interfering with the amine group package (3418 cm\(^{-1}\)) due to the hydrogen bond that occurs to both of them. The beam that appears at (2920 cm\(^{-1}\)) confirms the associated alkyl groups' presence and that the beam is at (1620 cm\(^{-1}\)). It refers to the carbonyl group in the amides, but at (1647 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. After adsorption process, the adsorption beams of the active groups present on the surface of the compound are shifted and decreased due to the hydrogen bonding with these groups [14, 15].

![Fig 1. FT-IR analysis for CH-g-poly(AAc-CO-Am) Before and after Zinc Oxid Adsorption.](image)

Using FE-SEM analysis shown that Hydrogel Poly (CH-(AAc-co-Am)) The microscopic images of hydrogels prove that they have porous structures, i.e., they have good sites for adsorption and the structure of the composite membranes with a crust a shape. The pores are interconnected. This is due to the strong bonding between the polymeric chains by the cross-linking agent and enhances the hydrogel's swelling rate. After adsorption, the images show the surface. The appearance becomes rough due to grafting with ZnO filling of the pores and the association of the adsorbed zinc oxide particles with the active centers of the adsorbent surface, and the ZnO particles are visible on the surface of the superimposed, and this indicates that the adsorption process has occurred [16-18].
Fig 2. FE-SEM for (Ch-g-poly (AA – co – Am)) after and before adsorption.

Using TEM analysis, Hydrogel Poly (CH-(AAc-co-Am)) has a small granule and uniform distribution. It has excellent dispersion, uniformly arranged, and agglomerate, which returns to the chitosan matrix. After adsorption, the poly (CH- (AAc-CO-Am)) is covered with heterocyclic nanobodies of zinc oxide molecules[19, 20].

The thermal behavior of the Chitosan-g-poly (AA – co – Am) compound has been studied by TGA, which measures the change in the sample mass within the thermal range (900-40) °C with a heating rate of 100C / min in the presence of gas nitrogen. Figure (3-10) shows that the prepared hydrogel compound is very stable within the temperature range of (97-0) °C and does not suffer breakage at this temperature range and when the temperature reaches the range of (97- 155) °C begins with a slight dissolution of 9.8 and is attributed To water molecules adsorbed on the surface, and when the temperature range reaches (260 -370) °C part of it is dissolved by (19.3%) 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 C-OC[21]. The temperature range is between (375-472) °C, the decomposition in it is at (46.3%), which is attributed to the thermal breakdown of the interlocking polymeric chains of the hydrogel complex[9, 15]

Table 1. Thermal decomposition values Ch-g-poly (AA – co – Am).

| Stage | TGA Range °C | Mass loss % | DTA(°C) |
|-------|--------------|-------------|---------|
| 1     | 40           | 0           | 105 (+) |
| 2     | 97-155       | 9.8         | 312 (+) |
| 3     | 260-370      | 19.3        | 415 (+) |
| 4     | 375-472      | 46.3        |         |
The external shape of the prepared surface was analyzed using atomic force microscopy, which gives a three-dimensional image of the shape of the sample. Statistical information can be obtained on the surface roughness values of Surface roughness, shown in Figure 5.

### Table 2. Statistical roughness coefficients for CH-g-p (AA – CO – Am).

| Chitosan-g-poly (AA–co–Am) | The statistical value of roughness |
|-----------------------------|-----------------------------------|
| 5.453                       | Roughness rate($R_a$) nm          |
| 6.621                       | Average square root of ($R_q$) nm roughness |
| -1.08                       | Torsion of the surface($R_k$)nm  |
| 3.856                       | Flat peaks($R_{4a}$)nm            |
| 10.30                       | The upper limit of the ($R_z$) nm height of the peaks |
| 24.85                       | Minimum roughness ($R_p$) nm depth |
| 35.14                       | The maximum height of the ($R_z$) rough surface |

**Figure 5.** 3D image of the atomic force microscope (CH-g-p (AA –co – Am))

**Adsorption Kinetics Study and Equilibrium Time Effect**

Through practical experiments, the kinetic models for absorption of zinc oxide were accurately determined on the union surface (Ch-g-poly (AA – co – Am)), by analyzing the two false pseudo-models of the first and second-order as in Figure (7). Where the kinetic
constants and correlation coefficients were calculated for the adsorption process as in Table (1-4), where it was observed that the value of (R2) for the second-order wrong model is much higher than the first wrong model, so the adsorption of the zinc oxide solution is of the first-order error [6, 22].

Fig 6. Effect of reaction time (A), pseudo-first-order (B), and the pseudo-second-order (C) on ZnO ion adsorption.

**Table 3.** Kinetic adsorption coefficients of zinc oxide on (CH-g-p (AA – CO – Am))

| Pseudo-first order ZnO | Pseudo-second order ZnO |
|------------------------|-------------------------|
| R² | qₑ (mg/g) | k₁ (min⁻¹) | Intercept | Slope |
| 0.5522 | 5.97629 | 0.0167 | 1.7878 | -0.0167 |
| h (mg g⁻¹ min⁻¹) | R² | qₑ (mg/g) | k₂ (g. mg⁻¹.min⁻¹) | Intercept | Slope |
| 2.088119 | 0.9966 | 15.67398 | 0.0085 | 04789. | 0.0638 |
4. Conclusion
A study of the Poly Ch-g-poly (AA – co – Am) was performed using zinc oxide. Due to the compound’s high adsorption activity, it can be used in biological activity as an inhibitor of bacteria and fungi. The results showed that the compound has an increased ability to adsorb zinc oxide through the results of (SEM-TEM) and adsorption from the Pseudo-second order model ($R^2 = 0.7766$) (comparative Pseudo-second order model ($R^2 = 0.7766$)).

5. References

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