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Characterization and Metal Sorption of PolyAcrylamide /Chitosan Nanocomposite Hydrogel Synsisyezed by Gamma Irradiation

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Abstract

Gamma irradiation was used to prepare nanocomposite hydrogels composed of polyacrylamide (PAM) and chitosan nanoparticles (CS-NPs). The hydrogels were investigated by FT-IR spectroscopic analysis, thermogravimetric analysis (TGA) and the measurements of swelling in water. The metal sorption and kinetics for Cu^{+2}, Pb^{+2} and Fe^{+3} metal ions was investigated. The results of TGA analysis showed that the PAM/CS-NPs hydrogels had lower thermal stability than PAM hydrogel. It was found that PAM and PAM/CS-NPs hydrogels reached the equilibrium swelling in water at 4 hours. However, PAM/CS-NPs hydrogels displayed higher swelling in water than PAM hydrogel. The metal sorption study showed that PAM/CS-NPs nanocomposite had high affinity and selectivity for the metal ions according to the order: of $Cu^{+2} > Pb^{+2} > Fe^{+3}$. On the other hand, the sorption by the hydrogel networks is controlled by applying Fick's law.

Keywords: Nanocomposite, Gamma radiation, Metal sorption, Selectivity

1.Introduction

Heavy metals are common water pollutants that come from industrialized areas where streams and rivers flow. Macro concentrations of heavy metals in water have a negative impact on the environment over time. They congregate in specific organs of animals and plants, causing biochemical balances to shift. Some biochemical reactions can thus be blocked or catalytically rerouted in undesirable directions. As a result, many organisms can fundamentally harm and alter the natural environment. many efforts have been done to overcome this problem. Chelating matrices are of the most important classes of solid phase extractors. The present attention is focused largely on designing stable chelating matrices with high binding constants, selectivity and capacity for metal ions. In this regard, hydrogels by its Three-dimensional network structures can swell and absorb large amounts of water or biological fluids, allowing for a wide range of industrial applications **[1]**.

Chitosan is one of the most abundant biopolymers, with great potential in hydrogel preparation. Many chemical modifications are being made to improve the utilization of chitosan. During this competition, chitosan functionalized with xanthenes as a highly enhanced adsorption for lead ions from battery wastewaters was reported **[2]**. The use of chitosan/magnetite composite beads in the removal of Pb(II) and Ni(II) from aqueous solutions was investigated **[3]**. Chitosan and poly(vinyl alcohol) films with different mass ratios were prepared to be used as Pb(II) removal devices **[4]**. Activated carbons, plant or lingo-cellulosic wastes, clays, and chitosan were used as adsorbents to remove dyes **[5]**. Fe_3O_4 magnetic nanoparticles (MNPs) modified with 3-aminopropyltriethoxysilane and acrylic acid/ crotonic acid copolymers were used to remove heavy metal ions (Cd2+, Zn2+, Pb2+, and Cu2+) from aqueous solution **[6]**. Removal of heavy metal ions with a hydrogel based on ethylenediamine tetraacetic acid (EDTA), crosslinked chitosan crosslinked polyacrylamide initiated by N,N-methylenebis (acrylamide) (MBA) was reported **[7]**. Different hydrogels based on crosslinked chitosan were prepared and used for metal uptake **[8]**. The results

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showed that the order of the selectivity of crosslinked chitosan derivatives toward metal ions was found to be Cu(II) > Cd(II) > Fe(II) > Co(II) > Ni(II). A semi-interpenetrating polymer network (semi-IPN) hydrogel was synthesized, by combining α-ketoglutaric acid grafting chitosan with polyacrylamide crosslinked by N,N-methylenebis (acrylamide), and for heavy metal ion removal [9]. It was found that the theoretical maximum adsorption capacities of Cu(II), Pb(II), and Zn(II) by the hydrogel were 72.39, 61.41, and 51.89 mg/g, respectively; however after five adsorption-desorption cycles, the adsorption capacity of Cu(II), Pb(II), and Zn(II) still maintained above 90% of initial adsorption capacity. Biopolymer-based hybrid hydrogels were developed to remove Cr (VI) ion from aqueous solution [10]. PVA/PVP/ST-g-AAm/CS/GO HH was prepared using poly(vinyl alcohol) (PVA), poly(vinyl pyrrolidone) (PVP), acrylamide-grafted native starch (ST-g-AAm), chitosan (CS), and graphene oxide (GO).

There is also an interesting in designing chelating matrices including a variety of organic and inorganic supports have been investigated. They include cellulose copolymers [11, 12] and resins of the Amberlite series [13- 20]. Silica gel was also used [21- 29]. In a previous work, the metal sorption of polyacrylic acid (PAAc) and sodium alginate (AG) based hydrogels synthesized by gamma irradiation was studied [30]. It was found that PAAc hydrogel had a higher affinity for Cu^{+2} ions than AAc/AG hydrogels. However, AAc/AG hydrogels had a stronger preference for Co^{+2} and Ni^{+2} ions than PAAc hydrogel. The sorption of metals and separation of some divalent metals by a new series of gamma-irradiated ionic polymer resins was studied [31]. So far, no research has been conducted on nanoparticle chitosan. In the present work, an interpenetrating hydrogels were created by gamma irradiating aqueous solutions primarily composed of polyacrylamide (PAM) and various ratios of nanoparticle chitosan (CS-NPs). An important goal of this work is to investigate the potential use of PAM/CS hydrogels in the treatment of toxic heavy metal-laden wastewater. As a result, the sorption kinetics of some divalent and trivalent metal ions, as in Cu^{+2}, Pb^{+2}, and Fe^{+3}, by PAM/CS hydrogels were also investigated.

Experimental

Materials and methods

Chitosan (CS) used in this study was of laboratory grade sourced from Aldrich Chemical Co. (Milwaukee, WI, USA) and implemented as received. Merck, Germany, supplemented Polyacrylamide (PAM) laboratory grade, which was utilized without further purification. Three metal salts, $CuSO_4$, $Pb(NO_3)_2$ and $FeCl_3$ were used for metal sorption studies. All the chemical reagents used were supplied by Merk Co., Germany.

Preparation of chitosan nanoparticles

CS-NPs were prepared according a reported method [32]. In this method, 0.5% w/v chitosan was pre-dissolved in 1% v/v acetic acid solution and was then put into test tubes and exposed to doses 5, 10, 15 KGy of gamma irradiation at ambient temperature After gamma irradiation, precipitated in 1% w/v sodium hydroxide to obtain white colloidal particles. The re-precipitate product was washed with distilled water several times and 0.5% w/v of the colloidal product was kept in distilled water. The sample CS-colloidal nanoparticles form was suitable for TEM measurement.

Preparation of PAM/CS nanocomposite hydrogels

The hydrogels were generated by dissolving different ratios of PAM and CS nanoparticles in distilled water separately. After that, the PAM and CS solutions were continuously mixed until complete miscibility was attained. The PAM/CS ratios in the combinations were 100/0, 75/25, 65/35 and 50/50 wt%. The mixtures were then poured into test tubes. The solutions were made free from oxygen by purging nitrogen gas for 5 min. Irradiation to the required doses (5–15 kGy) was carried out in a ⁶⁰Co gamma cell (made in Russia) facility of the National Center for Radiation Research and Technology, Cairo, Egypt, at a dose rate 2.81 KGy/h.

Transmission electron microscopy (TEM)

The formation of CS nanoparticles was examined by using transmission electron microscopy (TEM), model JEM 100CS, Joel electron microscopy, Japan. The TEM images were taken at 80 kV.

Gel fraction

Samples of the prepared nanocomposite hydrogels were accurately weighed (W_o) and then extracted with distilled water using a soxhlet system and then dried in a vacuum oven at 80°C to a constant weight (W_1). The gel fraction is calculated according to the following equation:

Gel fraction (%) = (W_1/W_o) x100

Swelling characters

Swelling of PAM/CS nanocomposite hydrogels in water carried out by immersing known dry weight (W_o) of samples in distilled water until equilibrium. The samples were then removed and blotted on filter paper to remove the excess of solution on the surface and weighed (W_2). The swelling (%) was calculated by employing the formula below.

Swelling % = $[(W_2 - W_o) / W_o]$ x 100

Scanning electron microscopy (SEM)

The morphology of the fracture surfaces of the copolymer hydrogels was accomplished by scanning

electron microscopy (SEM). The SEM micrographs were achieved with a JSM-5400 electron microscope made by Joel, Japan. A sputter coater was used to pre-coat conductive gold onto the fracture surfaces before observing the micrographs at 30 kV.

FT-IR spectroscopic analysis

The infrared analysis was carried out using the Unicam, England, Fourier-Transform Infrared Spectroscopy (FT-IR) model Mattson-Genssis over the range 400- 4000 cm-1 using KBr discs produced by combining KBr with fine powder of the polymer gel specimen and pressing in a hydraulic press (10:1 mass ratio of KBr to polymer).

Thermogravimetric analysis (TGA)

The TGA thermograms were done on a Shimadzu instrument TGA-50 (Kyoto, Japan) at a heating rate of 10ºC/min under flowing nitrogen (20 ml/min) from room temperature to 500ºC.

Sorption of heavy metals

Analytical determination of the different metal ions

A general procedure was used to determine the concentration of the different metal ions in solution based on measuring the light absorption of the colored solution specific for each metal [33]. In this method, a standard curve was first constructed for each metal ion under investigation, representing a relation between known different concentrations of the metal and the corresponding light absorption. These curves were used to determine unknown concentrations of the metal ions in solution by measuring light absorption. The light absorption measurements were performed with an UV/visible spectrophotometer (Unicam 8625 series). The wavelengths used for monitoring Cu, Fe and Pb are 324.8, 248.3 and 217.0 nm, respectively.

Determination of the distribution coefficient

The distribution coefficient (D) of the different metal ions was determined according to the flowing equation [33]:

$$D = \frac{\text{Concentration of metal ion in hydrogel}}{\text{Concentration of metal ion in filtrate}}$$

Determination of metal sorption

A dry weight (W_o) of The PAM/CS-NPs hydrogel immersed in constant concentration (mg/L) of the metal solutions $CuSO_4$, $Pb(NO_3)_2$, and $FeCl_3$. Metal uptake was calculated as follows:

Metal uptake (%) = $[(C_1 - C_o)/C_o]$ X 100

Where, C_o is the concentration of the metal solution before sorption and C_1 is the concentration after sorption by hydrogels.

Results and discussion

Formation of chitosan nanoparticles

The formation of chitosan nanoparticles was confirmed by transmission electron microscopy (TEM) as shown in **Fig.1**. The TEM micrograph indicated that the resultant product contains CS nanoparticles of a diameter range of (30–120 nm).
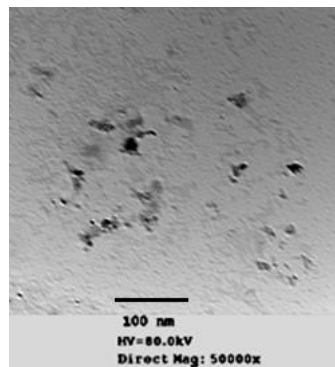

Fig.1. TEM images of CS nanoparticles.

Characterization of PAM/CS-NPs nanocomposites

Gel fraction

The effect of irradiation dose on the gel fraction (%) of different compositions of PAM/CS-NPs nanocomposite hydrogels is shown in **Fig 2**. The gel was gradually increased by the increase of the irradiation dose from 5 to 10 kGy and then tends to level off at higher doses. The increase of the CS-NPs ratio in the copolymer solutions, however results in decreasing the gel fraction. This finding could explain on the basis that CS-NPs undergo oxidative degradation at higher irradiation doses. The crosslinking of vinyl polymers such as PAM by ionizing radiation in solution has been established in radiation chemistry [34].
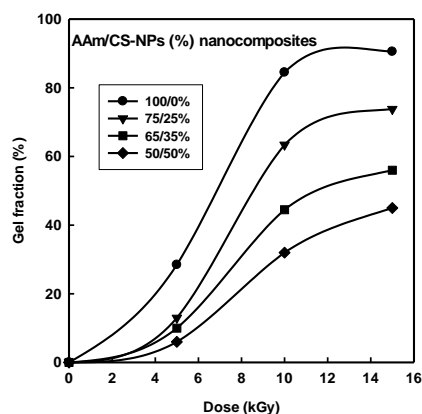

Fig.2. Effect of irradiation dose on the gel fraction (%) of different ratios of PAM/CS- NPs nanocomposites.

A semi-interpenetrating polymer network (semi-IPN) is defined as networks of two or more polymers, one of which is crosslinked and the other is present in non-crosslinked state inside the network [35]. Accordingly, it may be proposed that the formed

PAM/ CS-NPs hydrogel is a semi-interpenetrating polymer network (semi-IPN), in which CS-NPs polymer is physically entangled with the crosslinked PAM polymer as shown schematically in **Fig.3**.
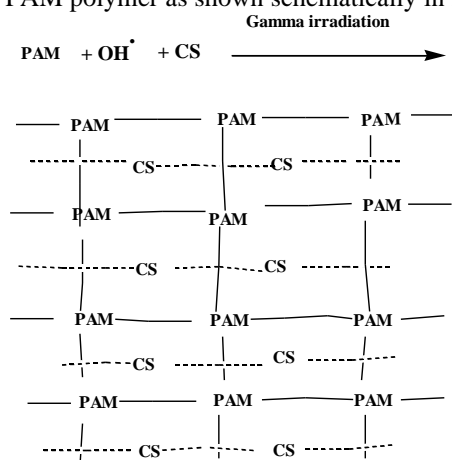
Gamma irradiation

$$PAM + OH^{\bullet} + CS \longrightarrow$$

Fig.3. Configuration diagram of semi- interpenetrating network structure of PAM/CS- NPs nanocomposite hydrogels.

Swelling characters

The effect of irradiation dose on the degree of swelling (%) of different ratios of PAM/CS-NPs nanocomposites is illustrated in **Fig.4.** The degree of swelling was found to increase with increasing irradiation dose up to 10 kGy and then become constant at higher doses, regardless of nanocomposite ratios.
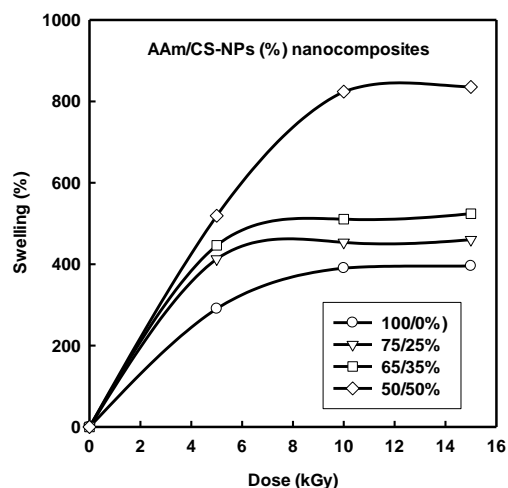

Fig.4. Effect of irradiation dose on the degree of swelling (%) at different ratios of PAM/CS-NPs nanocomposites.

This behavior is due to the occurrence of crosslinking and the formation of semi-interpenetrating polymer networks. PAM/CS-NPs nanocomposite hydrogels however exhibited higher swelling than pure PAM hydrogels. Meanwhile, the degree of swelling of PAM/CS-NPs hydrogels showed a regular behavior with respect to composition, in which the degree of swelling was seen to increase with increasing the CS-

NPs ratio. It is clear that the swelling increases as the crosslinking degree or the gel fraction decreases, in which the crosslinking make the structure more compact that prevents the diffusion of water onto the hydrogels.

Morphology characters

The morphology of the PAM/CS-NPs hydrogels was examined by scanning electron microscopy (SEM) as shown in **Fig. 5** for the fracture surfaces of PAM hydrogel and PAM/CS-NPs nanocomposites prepared, by gamma irradiation at a dose of 10 kGy.
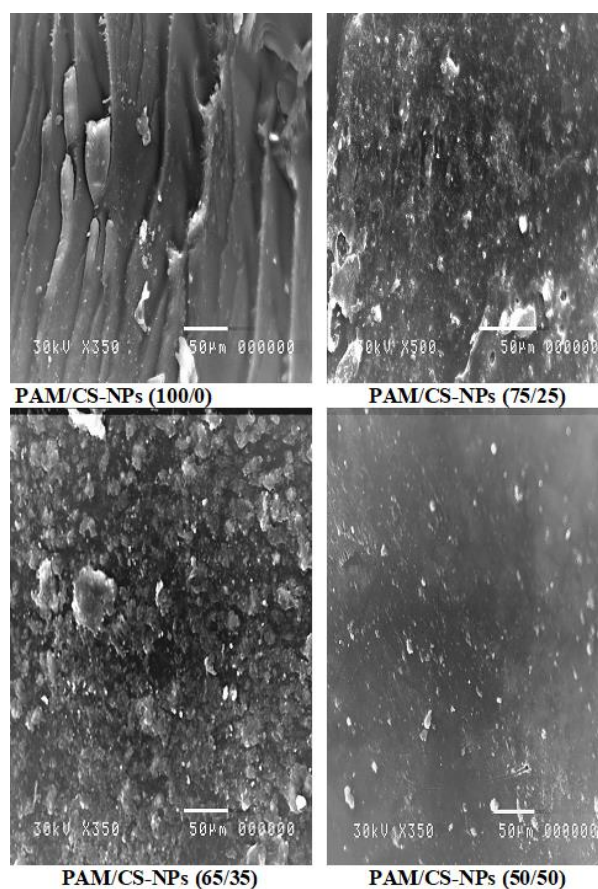

Fig.5. SEM micrographs of the fracture surfaces PAM hydrogel and PAM/ CS-NPs nanocomposites prepared at a dose 10 kGy of gamma irradiation.

The fracture surface of PAM hydrogel is characterized with the presence of wrinkles and folds indicating the occurrence of higher degree of crosslinking. The SEM micrographs of PAM/CS-NPs nanocomposite hydrogels, on the other hand, displayed a different surface morphology and the surface is characterized by the presence of roughness and changed with introducing CS-NPs in the hydrogels.

FT-IR spectroscopic analysis

The FT-IR spectra of PAM/CS-NPs hydrogels of different compositions formed by gamma irradiation to a dose of 10 kGy are shown in **Fig. 6**. An absorption peak around 2950 cm^{-1}, as well as a weak shoulder due to C-H stretching can be identified. In addition, an absorption peak at 1287 cm^{-1} can be detected due to the vinyl groups have. In the FI-IR spectra of chitosan, a characteristic absorption peak at 3500 cm^{-1} for hydroxyl groups can be identified. In addition, the absorption peaks at 1620 cm^{-1} and 1410 cm^{-1} arise from asymmetric COO_2 stretching vibration and symmetric COO_2 stretching vibration, respectively [36]. Furthermore, the FT-IR spectra of PAM/CS-NPs hydrogels revealed that the broadness of these absorption bands due to the hydroxyl was decreased with increasing CS-NPs ratio, indicating hydrogen-bonding formation. In this case, hydrogen bonding could formed between the $CO=NH_2$ groups of PAM and those of the COO_2 of CS-NPs.
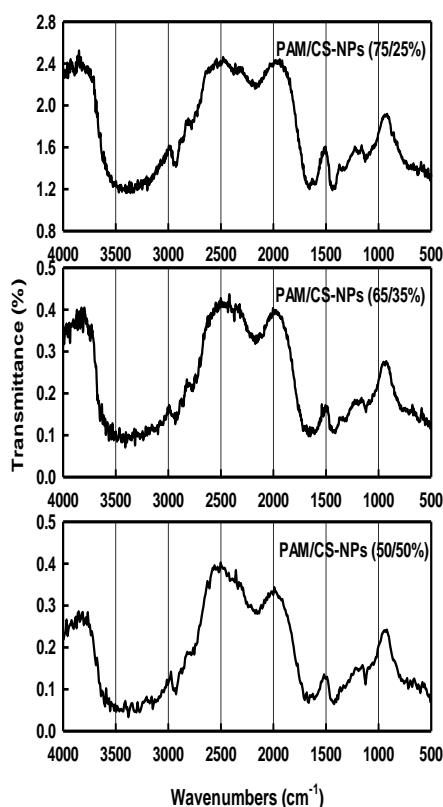

Fig. 6. FT-IR spectra of PAM/CS-NP snano-composites composed at different ratios prepared at a dose 10 kGy of gamma irradiation .

Thermal decomposition behavior

Figure 7 illustrates the TGA thermograms and the corresponding rate of the thermal decomposition reaction curves for PAM hydrogel and those for the PAM/CS-NPs nanocomposites of different ratios, prepared via gamma irradiation at a dose of 10 kGy. Two conclusions may be drawn from the TGA study:

Generally, gamma irradiation improves the thermal stability of PAM/CS-NPs, irrespective of composition.
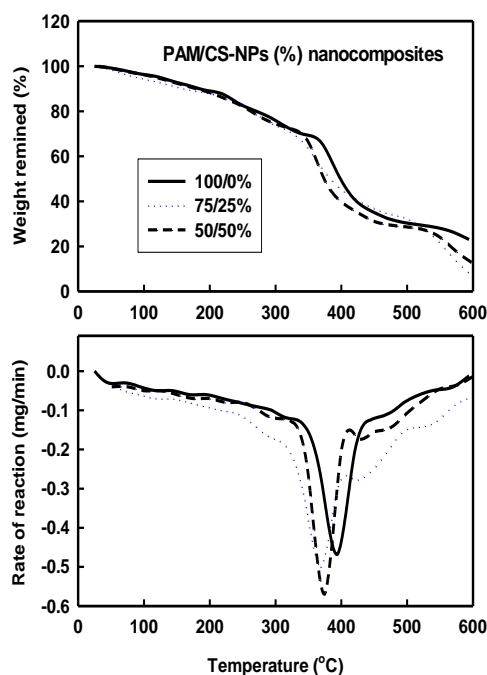

Fig.7. TGA thermograms and the corresponding rate of the thermal decomposition reaction curves for PAM hydrogel and PAM/CS-NPs nanocomposites at different ratios, prepared at a dose 10 kGy of gamma irradiation.

PAM hydrogel however demonstrated higher thermal stability than PAM/ CS-NPs hydrogels and that the thermal stability of PAM/ CS-NPs was found to decrease with increasing CS-NPs ratio. In this contest, CS-NPs have lower thermal stability than PAM. These finding could be explained according to the reported covalent bond dissociation energy that forms the molecules. PAM contains C=O groups (741 kJ/mol), whereas CS-NPs polymers have O-H groups (464 kJ/mol) [37]. As shown in **Fig.7**, all the hydrogels expressed similar curves of the rate of the thermal decomposition reaction, the temperature of maximum rate of reaction (T_{max}) depends on the hydrogel composition. The T_{max} of PAM, PAM/CS-NPs (75/25%), and PAM/ CS-NPs (50/50%) was determined to be 399.3, 374.7, and 374°C, respectively. Furthermore, the T_{max} was found to decrease as the CS-NPs ratio in hydrogel feeding solutions increased.

Metal sorption characters of PAM/CS-NPs nanocomposite hydrogels.

The metal uptake curves of different metals ions by CS-NPs (75/25%) nanocomposite hydrogel, fabricated through gamma irradiation at a dose of 10 kGy are shown in **Fig.8a**. Few points could be summarized from these curves:

(1) The main reactions between the ion metals are expected to occur through the -COOH and NH_2 groups of CS-NPs and PAM, in which replacement reactions would occur. These reactions govern to a great extend the affinity of hydrogels for metal uptake.

(2) The equilibrium metal sorption by PAM/CS-NPs nanocomposite hydrogels reached after 4 hours, regardless of metal ion type.

(3) The affinity of the PAM/CS-NPs hydrogel for Cu^{+2} is higher than Fe^{+2} and Pb^{+2} ions and explained accordingly to the electrochemical series activity. In this context, Cu^{+2} is beneath hydrogen in the direction of increasing strength of oxidation with standard reduction potential of +0.337 volts. Thus, H atom of COOH of CS-NPs is substantially replaced by Cu^{+2} than the other ions. Based on the standard reduction potentials, Fe^{+2} and Pb^{+2} metals are above hydrogen in the electrochemical series activity. So, sodium is more effectively replaced by Fe^{+2} and Pb^{+2} ions than the H atom of COOH in CS-NPs. In conclusion, the maximum uptake of different metal ions by pure PAM and PAM/CS-NPs nanocomposite hydrogel can be arranged as follow:

$Cu^{+2} > Fe^{+2} > Pb^{+2}$

(4) It is interesting; to calculate the slope of the initial straight-line part of the metal uptake-time curves for each metal (initial rate of metal uptake) as shown in **Fig.8b**. This property may be arranged as follow:
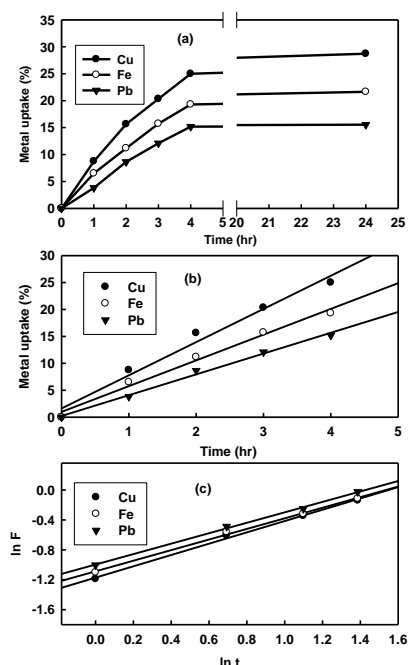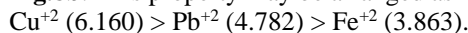Cu^{+2} (6.160) > Pb^{+2} (4.782) > Fe^{+2} (3.863).

Fig.8. Metal uptake and sorption kinetics curves of different metals ions by PAM/CS-NPs (75/25%) nanocomposite hydrogels, prepared at a dose 10 kGy of gamma irradiation.

(5) In separation science, the ratio of the distribution coefficients of the various metals (separation factor) was also considered. The greater the deviation of this factors from unity, the easier the separation. **Table 1** lists the distribution coefficient (D) and the rate of metal sorption and separation factor by PAM/CS-NPs (75/25%) nanocomposite hydrogels, prepared by gamma irradiation to the dose of 10 kGy. In this contest, the results showed that the PAM/CS-NPs nanocomposite has greater selectivity for Cu^{+2} than Pb^{+2} and much higher than for Fe^{+2}. PAM/CS-NPs nanocomposite, on the other hand, has higher selectivity for iron than lead.

Kinetic of metal sorption

The nature of the metal sorption characters of PAM/CS-NPs nanocomposite hydrogels nature was investigated using Fick's law **[38]**:
$F=W_t/W_e=Kt^n$
Alternatively,
$\ln F=\ln K + n \ln t$
Where W_t is the quantity of metal adsorbed by the hydrogel at time, **t** (seconds), and W_e is the quantity of metal adsorbed by the hydrogel at equilibrium, k is a constant characteristic of the network structure, and n is an exponent that determines the mode of the metal sorption. When $\ln F$ is plotted against $\ln t$, it produces a straight line, the intercept of which determines the constant K and the slope determines the number n. In this regard, a value of n = 0.5 indicates a Fickian sorption mechanism in which sorption is controlled by diffusion whereas a value of n = 0.5 indicates a Fickian sorption mechanism, in which sorption is controlled by diffusion. A value of 0.5 < n < 1 indicates non-Fickian sorption that contributes to the water-sorption process. The application of Fick's law to the metal uptake by PAM/CS-NPs nanocomposite hydrogels is shown in **Fig 8c**. The kinetic parameters of metal sorption by PAM/CS-NPs (75/25%) nanocomposite hydrogels, prepared by gamma irradiation to the dose of 10 kGy by applying Fick's law is illustrated in **Table 1.** Based on these data it can be noticed that the value of n is greater than 0.5 and < 1, indicating that the mechanism of metal sorption is non-Fickian regardless of metal. As a result, it is possible to conclude that the sorption by the hydrogel networks is controlled.

Conclusion

The present work reveals that chitosan, which is an abundantly available natural polymer, can be easily converted into good adsorbent for removal of Cu^{+2}, Pb^{+2} and Fe^{+3} metals from industrial wastewater. In this regard, gamma irradiation was successfully used to synthesize hydrogels based on polyacrylamide and chitosan nanocomposites. The results indicated that

PAM/CS have good thermal stability behavior. The metal sorption study showed that PAM/CS hydrogels showed high affinity and selectivity for the metal ions according the order: of $Cu^{+2} > Pb^{+2} > Fe^{+3}$. On the other hand, the sorption by the hydrogel networks is controlled by applying Fick's law. It can be concluded that the sorption by the hydrogel networks is controlled.

Conflict of interest
The authors declare no conflict of interest regarding the publication of this paper.

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