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Radiation synthesis of imprinted hydrogels for selective metal ions adsorption

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ABSTRACT

In this study, the imprinted hydrogels were prepared to remove cobalt and lead metal ions from wastewater with high selectivity. The imprinted hydrogel was prepared by copolymerization of (N-vinyl-2-pyrrolidone) and acrylamide monomers using gamma irradiation in the presence of cobalt or lead metal ions. The complexed ions were completely eluted with 2 M HCl. The control hydrogel was also prepared by similar experimental conditions without using imprinted ions. Both control and imprinted hydrogels were characterized by FT-IR, TGA XRD, and SEM. The effect of various parameters such as pH, time, and initial feed concentration on the extraction efficiency was investigated and compared data with control hydrogels. The pseudo-second-order kinetic model was described well the adsorption, reveals the good accessibility of the chelating sites in the imprinted sorbent for uptake of selected ion. The experimental data are fitted better to the Langmuir model ($R^2 > 0.99$) than the Freundlich model. It was found that the imprinted hydrogels were exhibited high affinity toward the template metal ions specially Pb^{2+}.

Keywords: Gamma-irradiation; Imprinted; Hydrogel; Metal ions; Selectivity

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1. Introduction

Hydrogels are cross-linked polymers that expand when in contact with a compatible solvent but cannot dissolve because of their cross-linked chemical structure. They derive their name from their affinity for water and the incorporation of water into their structures [1]. The hydrophilicity of the network is due to the presence of chemical groups such as (–OH), (–COOH), (–CONH–), (–$CONH_2$), (–SO_3H), and others that can be found within the polymer backbone. The presence of these functional groups, not only improves the water uptake capacity of the hydrogels, but these also act as efficient anchors for active molecular species and metal ions. The capacity of the hydrogels for metal uptake increases many folds with post functionalization by simple polymer analogous reactions. As hydrogels possess ionic functional groups, they can absorb and trap metal ions from wastewater [2]. Crosslinking can be achieved either by the addition of a crosslinker or by treatment of the polymer with high-energy radiation to induce polymer chain radical formation, and thus chain crosslinking [3]. The

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radiation technique seems promising for the preparation of hydrogels because it is simple procedure control, no initiators, crosslinkers, no waste, and relatively low operating costs make the irradiation technique a suitable choice for the synthesis of hydrogels [4].

The release of heavy metal ions into our environment poses a threat to human health as well as to the ecosystem and especially to people due to the toxicological effects on living organisms [5,6]. Owing to their severe toxic effects on living organisms, the treatment of industrial waste has been a strong concern as it continues to develop. Efforts have been made to treat the wastewater from heavy and toxic metal ions using polymers containing complexing molecule as an effective adsorbents [7,8]. Metal ion imprinted polymers (MIPs) have been widely reported for application in solid phase extraction, selective estimation, and as sensors because of enhancing the selectivity of these MIPs [9,10]. This technique allows the formation of specific recognition sites in macromolecules by the use of molecule templates which include drugs, hormones, pesticides, proteins, amino acids, peptides, carbohydrates, coenzymes, nucleotides, nucleotide bases, steroids, dyes, and metal ions. The application that promises to be of greatest industrial significance in the immediate future is that of molecular recognition materials for biosensors, highly specific catalysts, antibody for quantitative assay and molecular recognition, drug delivery, and tailor-made separation materials [11].

In this study, an imprinted hydrogel was prepared by gamma-radiation for uptake Pb^{2+} and Co^{2+} ions from the aqueous environment. (Acrylamide/2-vinylpyrrolidone) (AAm/NVP) hydrogel was chosen as a matrix for preparing imprinted molecule. The imprinted hydrogel was evaluated for the binding capability toward Pb^{2+} and Co^{2+} in the aqueous environment and compared with non-imprinted one. Factors such as pH, time, and initial metal ions concentration that affecting the uptake were carried out. The affinity or selectivity toward Pb^{2+} and Co^{2+} was also studied.

2. Materials and methods

2.1. Materials

The monomers used in this study, namely N-vinyl-2-pyrrolidone (NVP) and acrylamide (AAm) were supplied from (Merck, Germany) and used as received without further purification and their chemical structure are shown in Fig. 1. All other chemicals used such as metal salts and buffers were reagent grade and purchased from El-Nasr Co. for Chemical Industries (Egypt) and used as purchased without further purification. The bi-distilled water was used in all experiments.

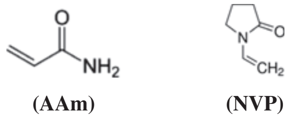

Fig. 1. The chemical structure of AAm and NVP monomers.

2.2. Preparation of (AAm/NVP) hydrogels

A known weight of (AAm) (20 g) was dissolved in distilled water to total volume 100 ml, also (20 ml) of (NVP) was taken and dissolved in distilled water to total volume 100 ml to prepare concentration of (20 wt %) from each monomer. Two compositions of AAm/NVP were prepared; 30/70 and 50/50 wt%. The homogenous solution of two monomers was transferred into the glass tube to be irradiated by ^{60}Co gamma source at room temperature and different radiation doses (10, 20, 30, and 40 kGy). After copolymerization, the vials were broken, the formed polymeric cylinders were removed, and cut into discs of 2-mm thickness and 5-mm diameter. All samples were washed in excess water to remove the unreacted component, then air dried at room temperature.

2.3. Preparation of AAm/NVP imprinted hydrogels

A solution of total monomers concentration 20 wt % of a composition 50/50 AAm/ NVP was prepared as mentioned above. 0.1 g of metal ions was added and the solution of total volume 10 ml was irradiated at irradiation dose 30 kGy. After irradiation, all samples were washed in mineral acid (2 M of HCl) to remove the metals and washed in excess distilled water to remove excess of mineral acid, then air dried at room temperature.

2.4. Gel fraction

The gel content in the dried samples was estimated by measuring its insoluble part after extraction in distilled water for 24 h at 70°C. Then, they were taken out and washed with hot water to remove the soluble part, dried, and weighed. The gel fraction was calculated according to the following equation:

$$\text{Gel fraction}\,(\%) = \frac{W_d}{W_0} \times 100 \qquad (1)$$

where (W_0) is the initial weight of dried sample and (W_d) is the weight of the insoluble part after extraction with water and air dried [12].

2.5. Characterization of the prepared hydrogels

Analysis by FTIR spectroscopy was done using (Nicolet Is-10 FT-IR, USA). X-ray diffraction measurements of the AAm/NVP hydrogel was recorded using a D8-advance XRD apparatus (Bruker, Darmstadt, Germany). All the diffraction patterns were done at room temperature under constant operating conditions. Shimadzu, Japan; TGA system of type TGA-50 was used for measurement of TGA. The nitrogen gas flow at constant rate was about 50 ml/min to prevent thermal oxidation processes of polymer samples. The heating rate was 10℃/min from ambient up to 600℃. The surface analysis was done by JEOLJSM-5400 scanning electron microscopy SEM, Japan.

2.6. Swelling behavior

The swelling percent of the hydrogel was determined by the gravimetric method. A clean, dried sample hydrogel of known weight was immersed in distilled water at room temperature at a suitable time interval. The hydrogel was removed and the excess water on the surface was removed by blotting quickly with filter paper and weighed. The swelling percent was calculated as follows:

$$\text{Swelling percent } (\%) = \frac{W_s - W_d}{W_d} \times 100 \tag{2}$$

where W_s and W_d are the mass of the swollen and the dried hydrogel, respectively.

2.7. Adsorption experiments

A stock standard of Co^{2+} and Pb^{2+} ions solutions of 1,000 mg/L was prepared by dissolving an appropriate amount of analytical grade salt in distilled water. The working solutions containing different concentrations of metal ions were prepared by stepwise dilution of the stock solution. The pH values were adjusted by the addition of 0.1 mol/L NaOH or HCl solution. A 20 ml of various metal ions concentrations were incubated with a known weight of the dried samples and allowed to equilibrate for different conditions. The aqueous solution was separated from the hydrogel at desired intervals and the residual concentrations of metal ions were determined by PerkinElmer atomic absorption spectrophotometer (Perkin Elmer model 2380). The amount of metal ions adsorbed per unit mass of samples was calculated using the following equation:

$$q_e\,(\text{mmol/L}) = \frac{(C_0 - C_e)V}{W} \tag{3}$$

where q_e is the adsorption capacity of the imprinted hydrogels (mmol/L); C_0 and C_e are the concentrations of the initial and equilibrium metal ions solution (mg/L), respectively, V is the volume of the aqueous solution (L) and W is the mass of dry hydrogels (g) [13].

3. Results and discussions

3.1. Preparation of hydrogel

When NVP and AAm monomers are irradiated with gamma rays, one of the double bonds of –C=C– on the monomers break by the effect of ionizing radiation hence free radicals are generated. These free radicals combined with each other to form (NVP/AAm) hydrogel as shown in Fig. 2. Many factors control the preparation condition such as irradiation dose, comonomer composition, and monomers concentration.

It is well known that the gelation and crosslinking greatly depend on the irradiation dose. The higher exposure dose means longer exposure time, which consequently prolongs the propagation step of the process of copolymerization leads to higher degrees of gelation and crosslinking [14]. Effect of irradiation dose on the gelation at different compositions of (AAm/NVP) hydrogel is evaluated by varying the total irradiation dose from 10 to 40 kGy during preparation of the hydrogel at the total monomer concentration of 20 wt% and the results are shown in Fig. 3. It can be observed that increasing the irradiation dose from 10 to 30 kGy leads to increasing the crosslink formation and the highest gelation percent is observed at 30 kGy, above this value the gelation percent is decreased. These may be due to the increase of decomposition rate by increasing the irradiation dose from 30 to 40 kGy.

The comonomer composition has a great influence on the gelation process. It is expected that one of the binary monomer may enhance the gelation process of the other monomer or vice versa. As seen in Fig. 3 that, the gel percent of the hydrogel increases with increasing AAm content into the comonomer feed solution. Due to AAm is well known as a higher crosslinked polymer by the effect of irradiation and it favors the formation of hydrogels even at a very low monomer concentration [15].

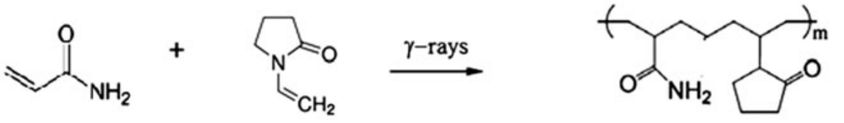

Fig. 2. Proposed scheme for preparation of (AAm/NVP) hydrogel.

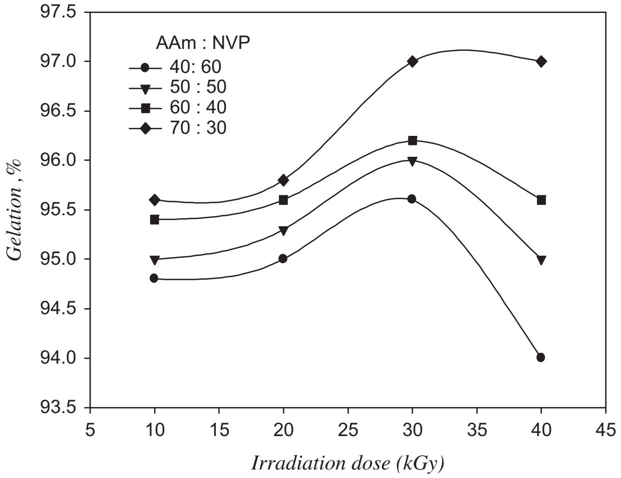

Fig. 3. Effect of irradiation dose on the gelation percent of (AAm/NVP) hydrogel at total monomer concentration 20 wt% and different comonomer compositions.

3.2. Preparation of Co^{2+} and Pb^{2+} imprinted hydrogel

The ion-imprinted polymer is obtained when a metal ion is used as template mixed with functional monomers. Better selectivity is achieved when polymerization is carried out with metal ions. The recognition properties due to the recognition sites within the polymer matrix are complementary to the template molecule in terms of the shape and positioning of functional groups. Once the template is removed, the resulting product is a crosslinked copolymer matrix with specific recognition elements for the template molecule [16]. The optimum conditions that obtained in the previous part were used in the preparation of Co^{2+} and Pb^{2+}-imprinted gel. The conditions for preparation of the imprinted gel are; the comonomer concentration is 20 wt% of (AAm/NVP) (1:1) at irradiation dose of 20 kGy that gives the best homogenous gel.

3.3. Characterization of the prepared hydrogels

3.3.1. FT-IR spectroscopy

Fig. 4 shows FT-IR spectra of the prepared non and imp(AAm/NVP) hydrogels of different compositions. FT-IR spectra of (AAm/NVP) hydrogels (Fig. 4(A) and (B)) show absorption peaks around 3,744 cm^{-1} arising from C–N group, 3,421 cm^{-1} arising from N–H stretch, 2,950 cm^{-1} arising from C–H stretching and –C=O stretching at about 1,654 cm^{-1}. The peak at 1,450 cm^{-1} arising from C–H bending of AAm. FT-IR spectra of the metal ions-imprinted hydrogel (Fig. 4(C) and (D)) show that there is a shift in the absorption band of –N–H group from 3,421 cm^{-1} to 3,394 for Co^{2+} and to 3,419 cm^{-1} for Pb^{2+} metal ions, whereas; the –C=O stretching peak is shifted from 1,653 cm^{-1} to 1,674 cm^{-1} in case of Co^{2+} and negative shift to 1,647 cm^{-1} for Pb^{2+}. The peaks in the region of 400–800 cm^{-1} can be assigned to the metal–imprinted stretching band.

3.3.2. Scanning electron microscopy (SEM)

Fig. 5 shows the surface morphological structure of (AAm/NVP) hydrogel with different compositions and the metal ions-imprinted hydrogels of composition (50/50). It can be observed that, the copolymer composition affects the hydrogel pore structure. As seen in Fig. 5, the (AAm/NVP) hydrogel of composition (50/50 wt%) shows a larger pore structure compared with the other composition (30/70 wt%) and this may affect the degree of swelling. The structural network of the (AAm/NVP) hydrogel of composition (50/50 wt%) has extensive surface area with a lot of cavities, which suggests better access to ions rebinding in the imprinted hydrogel cavities. This observation revealed that the introduction of NVP facilitates to improve the surface and network structure of hydrogel and the improved surface is convenient for the penetration of water into the polymeric network and is favorable to the enhancement of metal template ion absorption. Moreover, this observation also gives a direct revelation that NVP is almost embedded and dispersed within polymer matrix without coacervation [17]. For metal ions-imprinted hydrogel, it can be noted that, the surface morphology is changed compared with the surface of non(AAm/NVP) hydrogel. For Co^{2+} imprinted gel, the surface appears as coarse surface and roughness and some pores and gaps can be observed. This porous surface suggests better access to ions rebinding in the imprinted

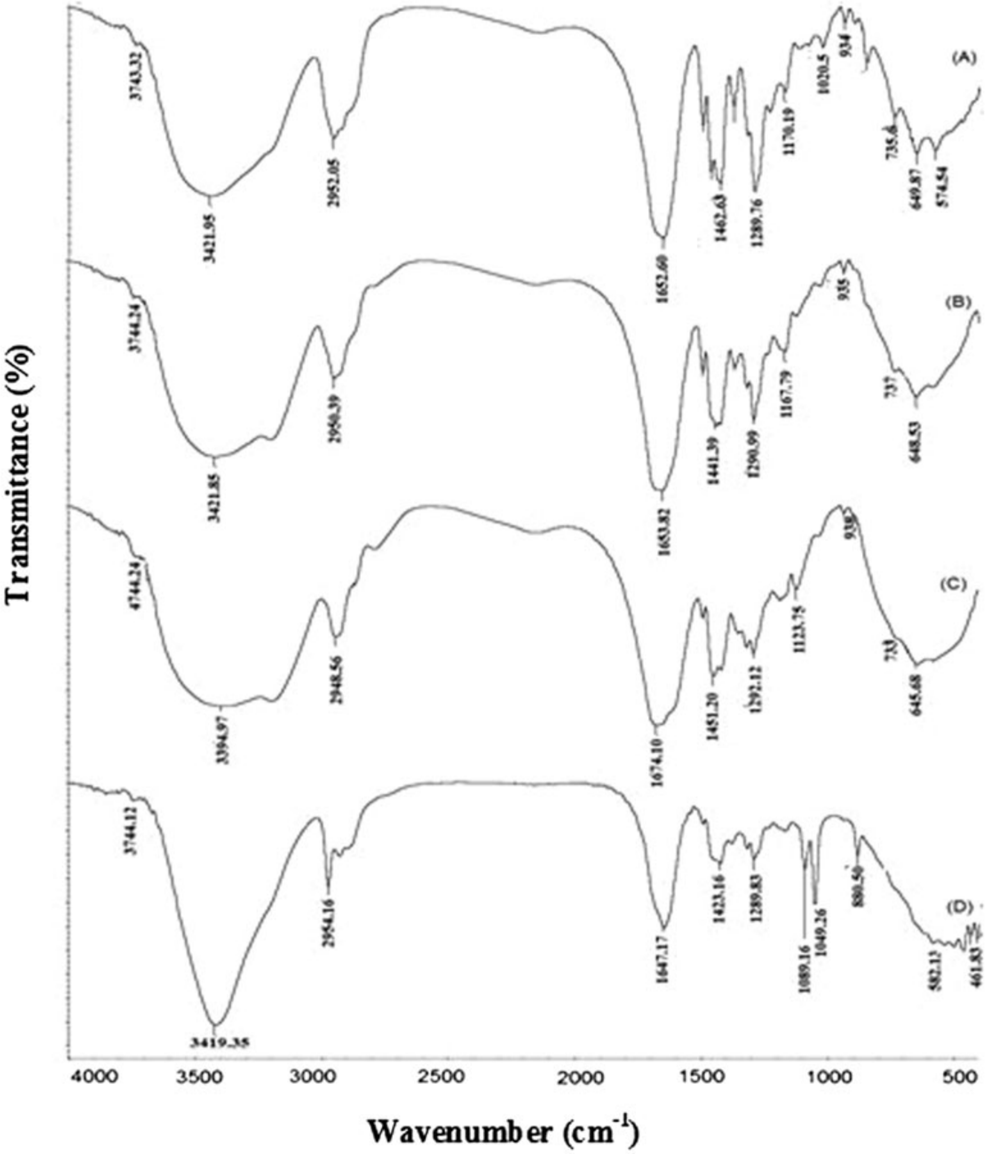

Fig. 4. FT-IR spectra of (AAm/NVP) hydrogel of composition 30/70 (A), 50/50 wt% (B), Co^{2+} (C), and Pb^{2+} (D) (AAm/NVP) imprinted hydrogel of composition 50/50 wt%.

hydrogel cavities. For Pb^{2+} imprinted gel, bright spots and rough surface are obtained. Smoothness of surface is observed compared with the surface of non (AAm/NVP) hydrogel.

3.3.3. Swelling behavior

The swelling property of hydrogel is an important factor concerned with its adsorption capacity. Fig. 6 shows the swelling percent of (AAm/NVP) hydrogel of various compositions and the metal ions-imprinted hydrogels of composition (50/50) as a function of time. It can be seen that the swelling percent is increased with an increase in the swelling time until the hydrogel is reached the equilibrium swelling state after 9 h for all investigated hydrogels. It can be also observed that the swelling percent is increased with an increase in the NVP content in (AAm/NVP) hydrogel or decrease in the AAm content. This can be explained by the fact that increasing the proportion of hydrophilic groups in the gel increases its affinity for water thus resulting in a greater swelling ability. The hydrophilic group on the NVP increases the number of hydrogen bonds formed with water, whatever, the swelling was increased [18]. On the other hand, the swelling percent was decreased with increasing AAm content in the feed mixture as a

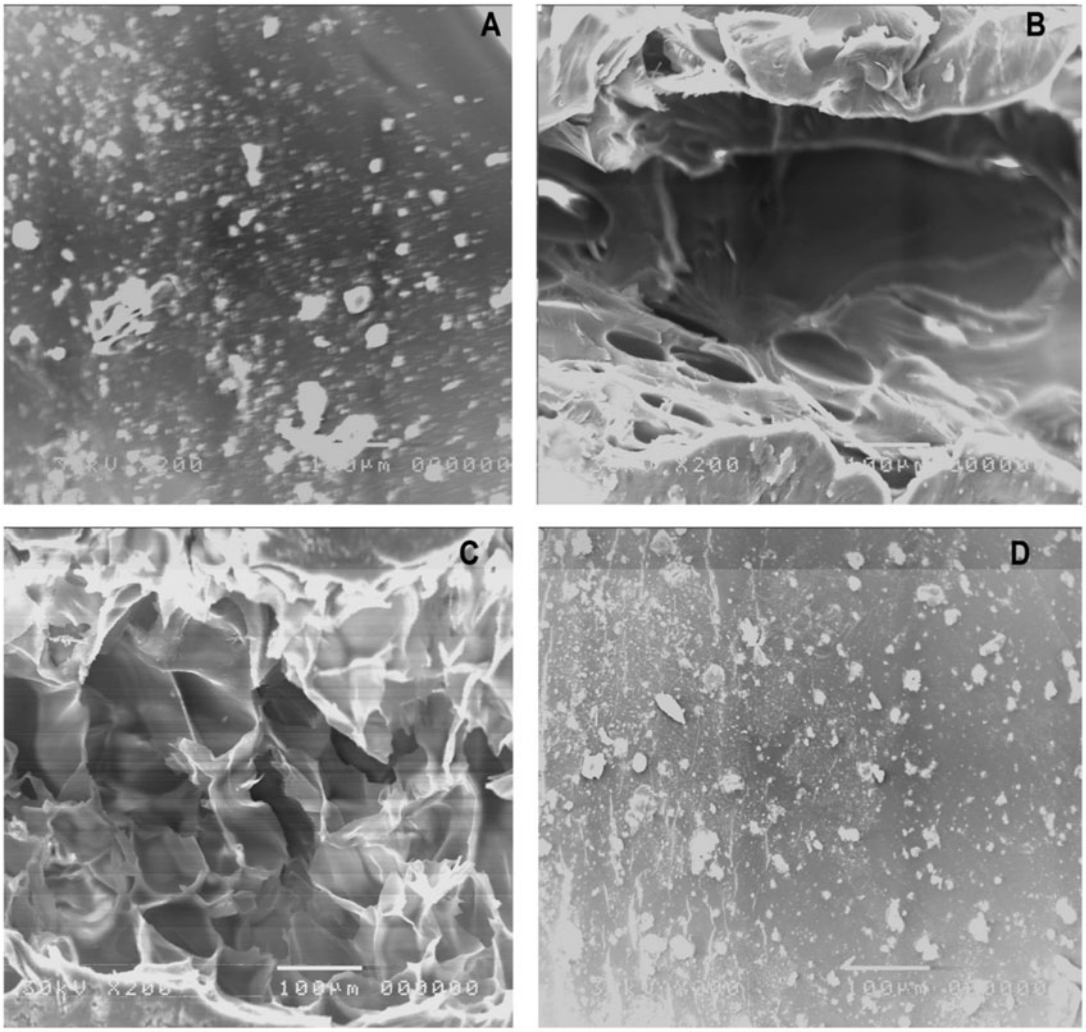

Fig. 5. SEM of (AAm/NVP) hydrogel of composition 30/70 (A), 50/50 wt% (B), Co^{2+} (C), and Pb^{2+} (D) (AAm/NVP) imprinted hydrogel of composition 50/50 wt%.

result of increasing the number of crosslinked polyacrylamide chains in the hydrogel network that leads to a decrease in the free volume and consequently lower swelling values [1]. For metal imprinted hydrogel, it can be noted that a little change in the swelling is observed compared with the non-imprinted hydrogel. By the way, the swelling percent increased for Co^{2+} imprinted gel while it decreased for Pb^{2+} imprinted gel due to the change in the porosity of the hydrogel that confirmed by studying the surface morphology in the previous section.

3.3.4. *Thermogravimetric analysis (TGA)*

The thermal behavior (AAm/NVP) and metal ions-imprinted hydrogels are investigated using TGA and shown in Fig. 7. The thermogram of (AAm/NVP) hydrogel for different composition shows three decomposition stages. The first step shows weight loss about 15 and 11% for compositions (50:50) and (30:70), respectively, within a temperature range of 50–220℃. These weight losses corresponding to the evaporation of water seem to depend on the presence and number of charges on the polymer chains. The major weight loss occurs in the second step up to 450℃ corresponding to the loss of ammonia by imidization and decomposition in the side groups. During the third stage, beyond 450℃ the weight loss is due to the main chain scission of polymer matrices which result in the rapid decomposition into carbon dioxide and volatile hydrocarbons. Results also show that the imprinted hydrogels with different metal ions are thermally

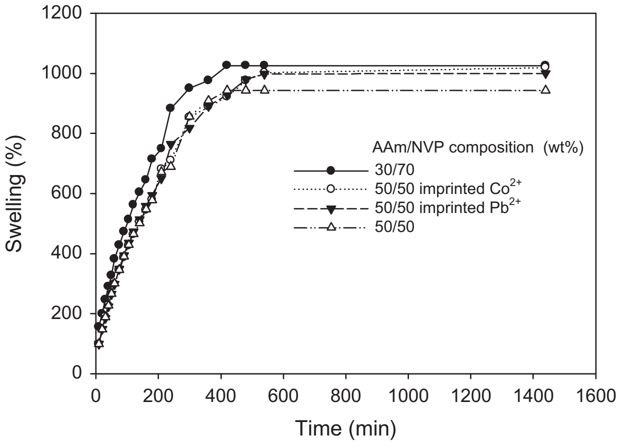

Fig. 6. Effect of time on the swelling percent of (AAm/NVP) hydrogels of composition 30/70 and 50/50 wt % and (AAm/NVP) imprinted hydrogel of composition 50/50 wt% with Co^{2+} and Pb^{2+}.

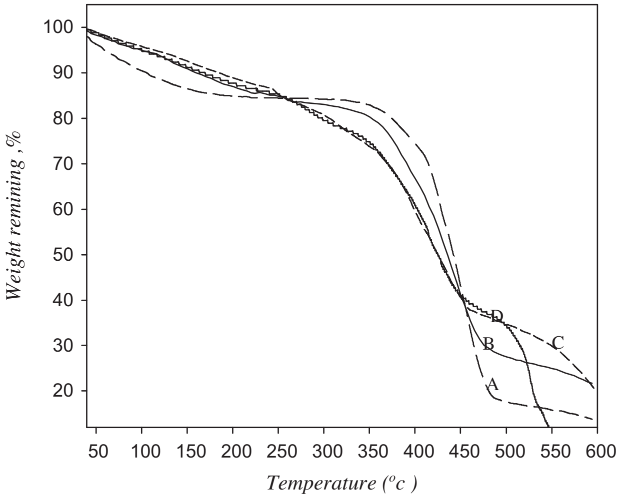

Fig. 7. TGA of (AAm/NVP) hydrogel of composition 30/70 (A), 50/50 wt% (B), Co^{2+} (C), and Pb^{2+} (D) (AAm/NVP) imprinted hydrogel of composition 50/50 wt%.

stable than unloaded one, which is suitable for most practical uses. It is observed that about 50% of (AAm/NVP) hydrogel weight is lost at temperature 410°C whereas; it is at 450°C for the hydrogels imprint with metal ions.

3.3.5. X-ray diffraction (XRD)

Fig. 8 shows the XRD of (AAm/NVP) hydrogels with different compositions and metal ions-imprinted ones at irradiation dose; 30 kGy. It shows that the hydrogel of composition (30:70) wt% has two wide peaks whose 2θ values are about 12.2° and 21° which are assigned to the diffraction of AAm and NVP, respectively [19]. With an increase of AAm content in the hydrogel as in composition of (50:50) wt%, there is an evidence for the formation of amorphous region in the hydrogel, as the broad signal only at 21° (2θ), this is due to an increase in the degree of crosslinking in the prepared hydrogel [20]. The diffractogram of (AAm/NVP) hydrogel is showed crystalline changes due to the effect of metal ion adsorption onto the polymeric matrix as shown in Fig. 8(c) and (d). The intensities of the diffraction peaks become intense and sharp, indicating that the reaction produced a new crystalline phase. That is, the complex has been formed in hydrogel loaded by metals ions, which all metal complexes show crystalline phase with a different degree of crystallinity [21]. The patterns at $2\theta = 16.62°$ and 17.27° support the formation of the crystalline region in the hydrogel due to Pb^{2+} and Co^{2+}, respectively, and the positioning of the ions in the crystal lattice [22].

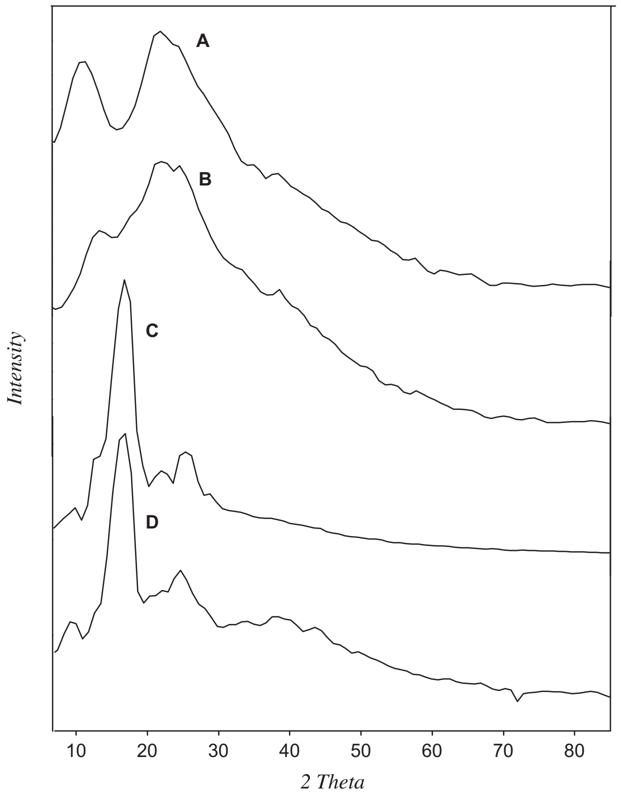

Fig. 8. XRD of (AAm/NVP) hydrogel of composition 30/70 (A), 50/50 wt% (B), Co^{2+} (C), and Pb^{2+} (D) (AAm/NVP) imprinted hydrogel of composition 50/50 wt%.

3.4. Adsorption study of the prepared hydrogels

Adsorption is one of the most common methods used in wastewater treatment. The main advantages of adsorption are; high efficiency, good selectivity, moderately high removal performance, cost-effectiveness, easy regeneration process of adsorbents, and sludge free treatment [23]. Factors affect the adsorption; such as pH, contact time, and initial metals concentration are evaluated.

3.4.1. Effect of solution pH

The effect of pH on the sorption of Pb^{2+} and Co^{2+} ions with the non and imp(AAm/NVP) hydrogel is investigated and shown in Fig. 9 by varying the solution pH from 2.0 to 7.0. It can see that, the extraction efficiency of the analyte increases significantly by increasing the pH of the sample solution up to pH of 5 which is due to the increase of bonding between polymer hydrogel and ion. Above this pH value, an decrease in the metal ions uptake is observed which may be due to precipitation of ions as hydroxide. Also, it can be observed that, the affinity of imp(AAm/NVP) hydrogel is higher compared with the non(AAm/NVP) one. In lower pH values, the nitrogen atoms of amide group may be protonated; and the metals-imprinted sites of the polymer are occupied by protons rather than ions. Higher pH values (>7) are not investigated because of the possibility of precipitation of Pb^{2+} and Co^{2+} ions as hydroxide [24]. Hence, the pH is adjusted to 5 in all subsequent studies.

3.4.2. Effect of contact time

The efficiency of hydrogels in waste treatment can be determined from the time required to adsorb the maximum capacity of metal ions by chelation with the functional groups. Fig. 10 shows the metal ions uptake as a function of contact time for non and imp (AAm/NVP) hydrogel. It can be noted that, the increase in contact time leads to an increase in the amount of metal ion adsorbed until the equilibrium is reached within 9 h. The results also show that, the ability of (AAm/NVP) hydrogel toward Pb^{2+} is higher than Co^{2+} ions. The maximum metal uptake of (AAm/NVP) hydrogel toward Pb^{2+} is 1.009 (mmol/g) but for Co^{2+} ions is 0.1174 (mmol/g). There are several possible explanations for this result, possible explanation for the differences in the absorption affinities might be related to differences in electronegativity (Pauling scale), being higher for lead (2.33) than for cobalt (1.88) metal with higher electronegativity behaves polar, being stronger attracted by investigated hydrogel. In addition, the hydrated radius of these metals, defined as the ionic radius together with its closely bound water molecules, is lower for Pb^{2+} (0.401 nm) than Co^{2+} (0.423 nm) with the lowest hydration energy for Pb^{2+} (−1,481 kJ/mol), with faster complex formation,which explaining why this pb^{2+} metal is preferentially absorbed despite its lower concentration [25]. As we can see in Fig. 9 that imp(AAm/NVP) hydrogel has higher adsorption capacity toward its template metal ion than non imp (AAm/NVP) one. The maximum metal uptake of imp (AAm/NVP) hydrogel toward Pb^{2+} is upgraded to

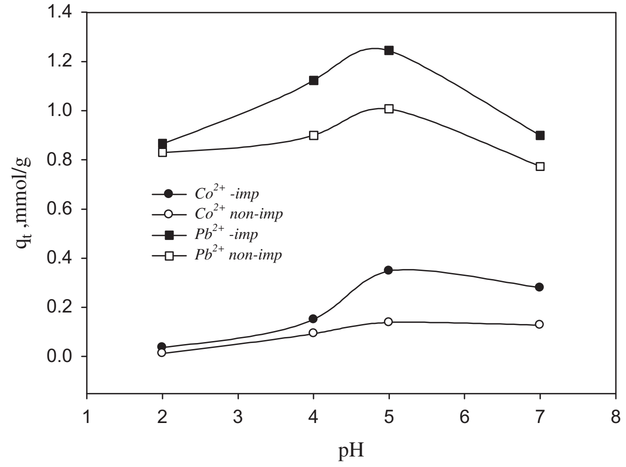

Fig. 9. Effect of solution's pH on the adsorption of Co^{2+} and Pb^{2+} at ambient temperature and initial metal ion concentration 500 mg/L.

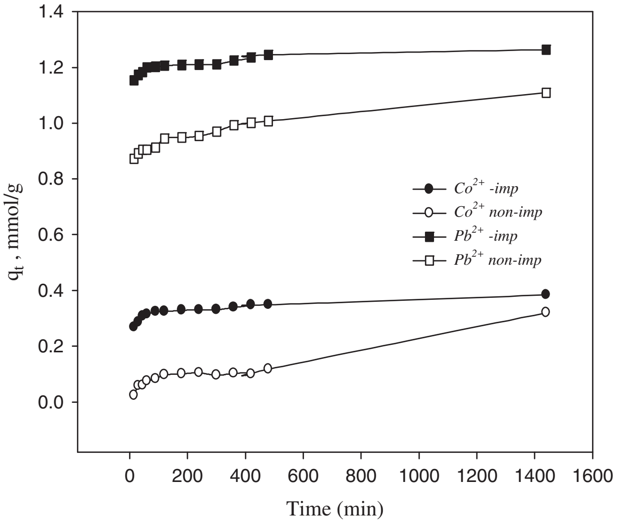

Fig. 10. Effect of contact time on the adsorption of Co^{2+} and Pb^{2+} at pH 5 and initial metal ion concentration 500 mg/L.

1.289 (mmol/g) but for Co^{2+} ions is to 0.3524 (mmol/g), which is confirmed the formation of the imprinted hydrogel.

3.4.3. Adsorption kinetics

Lagergren's pseudo-first-order equation is the earliest known one describing the adsorption rate based on the adsorption capacity. The linear form of Lagergren's pseudo-first-order equation is generally expressed as [26]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{4}$$

where q_e (mg/g) is the adsorption capacity at any time t (min); k_1 is the pseudo-first-order rate constant of the equation (min^{-1}). q_e is the equilibrium adsorption capacity (mg/g). The adsorption rate constant k_1 can be determined by plotting of log ($q_e - q_t$) vs. t.

The pseudo-second-order model, which is fit for the chemisorptions of metal ions onto adsorbents from aqueous solutions with polar functional groups. Pseudo-second-order equation is expressed as [27]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{5}$$

where k_2 (g/mg min) is the pseudo-second-order rate constant that is calculated by plotting t/q_t vs. t.

According to the intraparticle diffusion model proposed by Weber–Morris, the root time dependence may be expressed by the following equation [28]:

$$q_t = k_{id}t^{0.5} + C \tag{6}$$

where k_{id} is the intraparticle diffusion rate constant (mg g/min$^{-0.5}$).

The three modules are applied for the pb^{2+} and Co^{2+} adsorption by the non and imp(AAm/NVP) hydrogels and their parameters are all listed in Table 1. It can be found that, the correlation coefficients R^2 for the pseudo-second-order kinetic plots for all investigated studied are about 0.99, indicating that the pseudo-second-order kinetic model can describe well the experimental data. Therefore, the adsorption on investigated polymer hydrogels may be a chemical process through sharing electrons between the hydrogel and the metal ions.

3.4.4. Effect of initial concentration of metal feed solution

To investigate the effect of the initial concentration on metal ion adsorption, the process is carried out at different initial feed solution concentrations varied between 100 and 700 mg/L. The adsorption of Co^{2+} and Pb^{2+} is investigated in batch experiments at 27°C and pH 5.0 for 24 h to ensure equilibrium and the results are presented in Fig. 11. It is observed that the adsorption capacity of the hydrogels is increased with an the increase in the initial metal ions concentration until equilibrium occurs at 500 mg/L. This indicates that at lower initial metal ions concentrations, the adsorption sites on the hydrogel are sufficient; increase in the initial concentration can accelerate the diffusion of ions into the polymeric networks as a result of an increase in the driving force of concentration gradient. After a period of time, the remaining surface sites are difficult to be occupied. This is because of the repulsion between the solute molecules of the solid and bulk phase. Vacant sites depletion result in the adsorption capacity as the initial concentration reaches a certain limit [29]. A little decrease in the adsorption capacity for Co^{2+} imp(AAm/NVP) hydrogel above initial metal ions concentration 500 mg/L due to the competition and high repulsion between metal ions.

3.4.5. Adsorption isotherms

In this study, two typical isotherms are used for fitting the experimental data: The Langmuir adsorption model is applicable to homogeneous binding sites and assumes that the molecules are adsorbed at a fixed number of well-defined sites, each of which can only hold one molecule. The Langmuir equation could be expressed in the linearized form as:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{b\,q_{max}} \tag{7}$$

where q_{max} represents the maximum amount of adsorbed metal ions on the gel (mg/g), and b is the the Langmuir model constant of (L/mg) [30].

The Freundlich model is employed to describe heterogeneous system. The heterogeneity factor of $1/n$ is a measure of the deviation from linearity of the adsorption, if the value of $1/n$ is equal to unity, the adsorption is linear; if the value is below unity, this implies that adsorption process is chemical; if value is above unity; adsorption is a favorable physical process. The more heterogeneous the surface, the

Table 1
Coefficients of different kinetic models for Co^{2+} and pb^{2+} ions adsorbed onto non and imp (AAm/NVP) hydregels

Model	Parameters	Co^{2+} non	Co^{2+} imp	Pb^{2+} non	Pb^{2+} imp
Pseudo-first-order	k_1 (min^{-1})	1.15	1.73	0.81	1.87
	q_e (mmol/g)	0.081	0.114	0.102	0.056
	R^2	0.95	0.94	0.93	0.96
Pseudo-second-order	K_2 (g/mmol min)	1.54	0.352	0.35	0.86
	q_e (mmol/g)	0.129	0.68	0.97	1.22
	R^2	0.99	0.99	0.99	0.99
Intraparticle diffusion	K_{id} (mmol/g min$^{1/2}$)	0.0033	0.0029	0.0068	0.014
	C (mmol/g)	0.042	0.28	0.85	1.75
	R^2	0.84	0.85	0.98	0.79

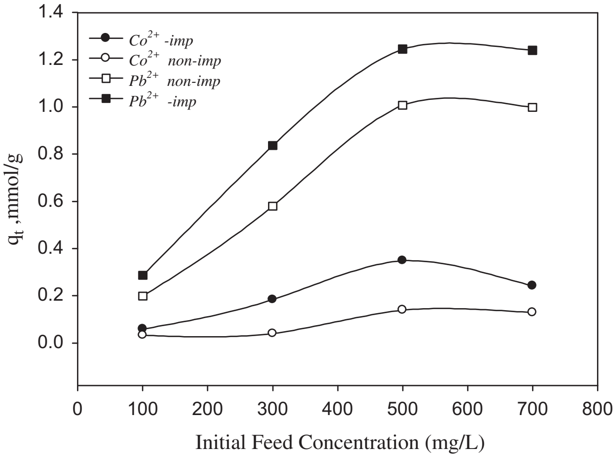

Fig. 11. Effect of initial metal ion feed solution concentration on the adsorption of Co^{2+} and Pb^{2+} at pH 5.

closer 1/*n* value is to 0 [31]. The Freundlich model is expressed as follows

$$\log q_e = \log k_f + \log C_e \tag{8}$$

where k_f is the Freundlich isotherm constant and 1/*n* (dimensionless) is the heterogeneity factor. The Langmuir and the Freundlich model are applied for adsorption of Co^{2+} and Pb^{2+} onto non and imp(AAm/NVP) hydrogel and the obtained data are summarized in Table 2. The experimental data are fitted better to the Langmuir model ($R^2 > 0.99$) than the Freundlich model, indicating that the adsorption of Pb^{2+} and Co^{2+} on investigated hydrogels is Langmuir monolayer adsorption. This may be due to the chelation between the $–NH_2$ groups and the metal ions on the hydrogel surface [32].

3.4.6. Competitive Sorption of $pb^{2+}$and Co^{2+} by the imprinted hydrogel

A comparative study is made for (AAm/NVP) hydrogel imprinted with Co^{2+} or Pb^{2+} to show the selectivity imp(AAm/NVP) hydrogels. The effect of imprinted molecule on the selectivity when Co^{2+} and Pb^{2+} ions exist in the same solution of total solution concentration 500 mg/L was studied. We obtained that the Co^{2+}-imp(AAm/NVP) shows higher affinity toward Co^{2+} than Pb^{2+}. However, Pb^{2+}-imp(AAm/NVP) possesses higher affinity toward Pb^{2+} than Co^{2+}. The Co^{2+}-imp(AAm/NVP) was adsorbed about 0.3815 mmol/g of Co^{2+} and 0.2310 mmol/g of Pb^{2+}. These results considered good results because non imprinted hydrogel has very higher capacity for Pb^{2+} than Co^{2+}. Although this consideration and unequal

Table 2
Coefficients of different isotherms models

Model	Parameters	Co^{2+} non	Co^{2+} imp	Pb^{2+} non	Pb^{2+} imp
Langmuir	q_m (mmol/g)	0.03	0.063	0.14	0.15
	$b \times 10^2$ (L/mmol)	0.15	0.15	0.30	0.41
	R^2	0.99	0.99	0.99	0.99
Freundlich	$K_f \times 10^3$ (mmol/g(L/g)1/n)	0.52	1.32	31.40	19.30
	1/n	0.92	0.86	1.3	0.88
	n	1.09	1.16	0.8	1.15
	R^2	0.97	0.98	0.98	0.97

competitive between two ions, this imprinted hydrogel prefers Co^{2+} rather than Pb^{2+}. For Pb^{2+}-imp(AAm/NVP) hydrogel, it was adsorbed about and 1.2012 mmol/g of Pb^{2+} and 0.1130 mmol/g of Co^{2+}. This means the Pb^{2+}-imp(AAm/NVP) hydrogel possesses a very high selectivity toward Pb^{2+} than Co^{2+}. The presence of template ion ensures relatively higher availability of the functional groups, which are complexed to the template ion during the imprinted hydrogel synthesis.

4. Conclusions

The affinity and selectivity of (AAm/NVP) toward Co^{2+} and Pb^{2+} ions were improved by imprinting of (AAm/NVP) using Co^{2+} and Pb^{2+} ions. The preparation conditions were studied, and the optimum conditions for preparing the imprinted gel are a comonmer concentration of 20 wt% of (AAm/NVP) (1:1) and at irradiation 20 kGy. It was found that, the imprinted hydrogels with different metal ions are thermally stable than unloaded one, which is suitable for most practical uses. Sorption of non and imp(AAm/NVP) Co^{2+} and Pb^{2+} ions onto non and imp(AAm/NVP) Co^{2+} and Pb^{2+} from their respective individual solutions were studied. It was demonstrated that, the optimum pH for both Co^{2+} and Pb^{2+} was found to be around pH 5. The pseudo-second-order kinetic model can describe well the experimental data. The experimental data are fitted better to the Langmuir model than the Freundlich model, indicating that the adsorption of Pb^{2+} and Co^{2+} is Langmuir monolayer adsorption. The Co^{2+}-imp(AAm/NVP) has selectivity toward Co^{2+} and Pb^{2+}-imp(AAm/NVP) has a very high selectivity toward Pb^{2+} from a solution contains both ions.

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