Fabrication of A novel polyvinylpyrrolidone/abeitic acid hydrogel by gamma irradiation for the recovery of Zn, Co, Mn and Ni from aqueous acidic solution

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Research Article

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Abstract

As heavy metals are a group of pollutants that originate from industrial and nuclear facilities has become of major concern in the aquatic environment due to their toxicity to all living organisms. In this context; this study was aimed to prepare sustainable and efficient hydrogel for the removal of heavy metals such as Co, Ni, Zn and Mn from aqueous acidic solution. The polyvinylpyrrolidone (PVP)/abietic acid (AA) hydrogel were prepared by gamma irradiation at 50 kGy. The characterization of PVP/AA hydrogel were investigated by water absorbancy, gel content, scanning electron microscopy, X-ray diffraction (XRD) and Fourier transform infrared (FTIR). The characterizations indicate that bio-sorbent composite hydrogel networks provide advantageous over conventional preparation techniques. PVP/AA hydrogel was implanted for batch process with studying the effect different parameters on the sorption of the investigated metal ions such as radiation dose; pH, contact time, metal ions, V/m and temperature. The results illustrate that the highest uptake% was obtained at radiation dose 30 kGy at optimum pH=3. The maximum adsorption capacity of PVP-AA adsorbent was reached 32, 32.5,19 and 32.5 $mg.g^{-1}$ for Zn(II), Co(III), Ni (III) and Mn(II) ions respectively. The changes in the values of free energy (ΔG) and enthalpy (ΔH) confirm the spontaneous nature of the adsorption reaction with an endothermic process. The maximum desorption of the investigated metal ions was achieved with 1 M HNO_3 of (97%, 98%, 70% and 60%) and takes the order: Co>Ni>Zn>Mn. The highest separation factor for Zn/Co=26 and Zn/Ni=8.6 at pH=0.75.

Keywords: PVP/AA; hydrogel; radiation; nickel; manganese.

1. INTRODUCTION

Recently, hydrogels have attracted a growing interest of many scientists in different fields of research and applications. Intelligent hydrogels have found a potential role in

various applications such as drug delivery systems; optics, diagnostics and imaging as well as process separations of metal ions [1], Hydrogels are defined as networks of cross-linked hydrophilic polymers capable of absorbing and releasing large amounts of water, while maintaining their structural integrity. These hydrogels are characterized with three dimensional networks, which enable the transport of ions, particles or other molecules while preserving on their structure during external stimuli. Polyvinylpyrrolidone (PVP), a water-soluble, non-toxic, non-ionic amorphous polymer with high solubility in polar solvents, has been widely used in nanoparticles synthesis [2]. Due to the amphiphilic nature, PVP can affect morphology and nanoparticle growth by ensuring solubility in various solvents, discriminatory surface stabilization, controlled crystal growth, playing the role of a shape-control agent and facilitating the growth of specific crystal faces while preventing others [3–5]. Abietic acid (AA) is a natural polymer, solid and brittle obtained from pine trees, and its derivatives have attracted much interest in the field of pharmaceutical applications due to their characteristic properties such as biocompatibility, biodegradability, low cost, and capable of chemical modifications due to their special structure [6]. They have also been used in the fields of cosmetics, adhesives, medicines, chewing gum, and dental varnishes [7]. Moreover, rosin can be proposed in order to prepare a matrix for silver nanoparticles to apply as antibacterial filler for wooden furniture or air filter for indoors, a catalyst carrier with potential application as counter electrode for dye-sensitized solar cells [8], a coating for bentonite particles and support for ferric oxide nanoparticles for chromium ions adsorption, [9] and activated carbons. On the other hand, Aba, an abietane diterpenoid, has shown antiallergic anti-inflammatory, phytoalexin-like, antimicrobial [10].

Different materials such as composites, natural and eco-friendly sorbent [11], nano-oxides [12], cryeptomylene [13], Nanomagnatite [14], hydrogels [15-16], Membrane bioreactors [17] and activated carbon [18] were employed for recovery and removal of heavy metals and toxic materials. Tea fiber was employed for the removal of nickel, zinc, cadmium, copper and lead from wastewater and the experimental results indicate that the data were matching better with the Freundlich model compared to other models [19]. The recovery of Mn, Cd, Ni and Co from leach solution (PLS) obtained from a sulphuric leaching process applied to unsorted spent batteries was carried out using Cyanex 272 and DEHPA by solvent extraction. The authors

concluded that Cyanex 272 and D2EHPA were proved as effective agents for the selective recovery of individual metal [20]. The use of γ -Irradiation in the preparation process is due to it's a clean and rapid technique for polymerization process of different materials which used before for the improving of adhesive property and antibacterial activity of blend polymer (abietic acid-EVA) [21]. One of the recent environmental requirements it's to recover and remove heavy metals and other toxic materials which present in fission product or other industrials waste streams using sustainable, eco-friendly and economic materials (green chemistry). From this point, in the current study a promising PVP-AA hydrogel blend was prepared via gamma irradiation technique and implanted for the recovery of cobalt, nickel, zinc and manganese from aqueous acidic nitrate solution. The synthesized hydrogel adsorbent was characterized using different techniques such as SEM, FT-IR and XRD. PVP-AA adsorbent was used for batch adsorption experiments with detailed study for various parameters which affect the recovery process such as radiation dose, pH, metal ion concentration and temperature effect. Desorption investigations for the loaded metal ions from PVP-AA hydrogel adsorbent were also carried out.

2. Experimental

2.1. Materials

Polyvinylpyrrolidone (PVP); Mw 25,000 g/mol was purchased from Merck, Germany. Abietic acid (AA) with melting point 173^{o}C and molar mass 302.458 g mol^{-1} was supplied by HAB Co., Delhi, India. Both polymers were used without further purification. Sodium hydroxide (NaOH); Mw 40, purity 99%) was purchased from El- Nasr Pharmaceutical Chemicals Company, Egypt.

2.2. Preparation of PVP/Aba hydrogels

The PVP/Aba hydrogels were prepared by dissolving technique using distilled water at a temperature of 70°C. Firstly, 5g of Aba was dissolved in 10 ml of distilled water at 70°C, and pH 8 by using a mechanical stirrer at 60 rpm (round per minute) for 30

min. After the completion solubility of Aba (solution), the PVP/AA hydrogels were obtained by mixing of PVP in the solution by using a mechanical stirrer till a homogenous mixture of PVP/Aba mixture is obtained. The following PVP/Aba hydrogels ratios (w/w) were blended: 1/1, 2/1 and 1/2. The blends were exposed to γ-rays for a dose ranged from 10-50 kGy, using a cobalt-60 source of gamma radiation manufactured in Egypt's MEGA, gamma I, supplied by the Atomic Energy of Canada with a dose rate of 1.66 kGy/h, in the National Center for Radiation Research and Technology Cairo, Egypt.

2.3. Characterizations and Measurements

X-ray diffraction (XRD) was recorded using a Shimadzu diffractometer, XRD-6000 x-ray diffraction spectrometer with a copper target (λ = 1.542 A^o), at an operating voltage of 40 kV and an electric current of 30 mA. The pattern was recorded at a scanning rate of 4 step/min with an angular range (2θ) of 10^o –90^o.These operating conditions were sustained all through the examination.

Fourier transform infrared (FTIR) spectroscopy (a Nicolet Avatar 320 FT-IR Spectrophotometer, Cambridge, UK) with wave numbers ranging from 4000 cm^{-1} to 400 cm^{-1} was used.

Scanning electron microscopy (SEM) and EDX-mapping, the surface of the samples was examined by SEM (Jeol, JSM, Japan) at a voltage of 30 kV. The surfaces were pre-coated with a thin gold layer in order to reduce charging in the SEM.

Water absorbency measurement

The dry sample was weighed and immersed in water for 24 h to reach absorption equilibrium. The swollen gels were withdrawn at regular time intervals from the water, and weighed after removal of excess surface water by light blotting with a filter paper. Thus, the degree of swelling was calculated as gram of water per gram of polymer (g/g) from the following equation [14]:

$$\text{Degree of swelling (g/ g)} = \frac{W_s - W_d}{W_d} \times 100 \qquad (1)$$

Where W_s and W_d are the weights of the swollen gel and dry sample, respectively.

Gel Content

To extract the insoluble parts of the hydrogels (i.e., the gelled part), the prepared hydrogels were soaked in water for 24 h at 60 °C. Then, they were taken out and washed with hot water to remove the soluble part, dried, and weighed. The gel percentage in the hydrogel was determined from the following equation [14]:

$$Gel\ \text{Content}\ \% = \frac{W_a}{W_b} \times 100 \qquad (2)$$

where, W_a and W_b represent the weights of the dry hydrogel after and before extraction, respectively.

2.4. Sorption studies

The aqueous solution of Zn, Co, Mn and Ni were prepared from $Ni(NO_3)_2 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 4H_2O$, $Mn(NO_3)_2 \cdot 4H_2O$ purchased from Alpha chemicals (India) in double-distilled water and the desired diluted solutions with different pH values was prepared and adjusted using diluted nitric acid.

The Batch sorption experiments of Zn, Co, Mn and Ni from acidic nitrate medium on the potential PVP-AA adsorbent were investigated. In this manner, different parameters such as pH, contact time, V/m, radiation dose and temperature were examined by shaking 0.1 g of the PVP-AA adsorbent with 5 ml of 100 mgL^{-1} of the investigated metal ions in aqueous solution in thermostatic water bath shaker. After adsorption equilibrium attendance the concentration of Zn, Co, Mn and Ni was determined using PAR method [22] and the all the reported experimental results was an average of two duplicate experiments.

The uptake percent (Uptake %) of metal ions, the adsorption capacities at equilibrium (q_e, mg/g) and at any time t (q_t, mg/g) on PVP-AA adsorbent were calculated using the following equations respectively [23-24] :

$$Uptake\ \% = \frac{C_O - C_e}{C_O} \times 100 \qquad (3)$$

$$q_e = (C_o - C_e) \times C_o\ V\ /\ m \qquad (4)$$

$$qt = (C_O - C_t)\ \times C_O\,(\text{V/m}) \qquad (5)$$

Where C_o, C_e and C_t are the initial, equilibrium and at time t of the metal ions concentration respectively in the aqueous solution (mg/L); V is the volume of the solution (L); and m is the mass of the adsorbent (g).

3. Results and discussion

3.1. Water absorbency studies

Fig. 1 shows the effect of irradiation dose on water absorbency of PVP/AA hydrogel. The results indicated that the hydrogel swelling enhanced as the irradiation dose increased up to 30 kGy, then decreases until it reaches almost the same value of absorbency at 50 kGy. At low irradiation doses (below 30 kGy) the reduction in water absorbance may be due to the possible degradation in crosslinking density. This trend copes up with the outcome results of gel content. Further, at high doses (above 30 kGy), the PVP/AA formed a high percentage of crosslinking which could lead to the forming of narrow pores in the hydrogels causing not enough space for water molecules to enter the polymer networks, resulting in a lower water absorbency. Therefore, there is an ultimate crosslink content to maximal water absorbency.

3.2. Gel Content

Gel content indicates the degree of crosslinking formed in the hydrogel. A high degree of crosslinking will make the structure become rigid and reduces the ability of the hydrogel to absorb water. Fig. 2 illustrates the relationship between the gel content and the irradiation dose. The gel content (%) rises as the irradiation dose increases until reaching a maximum stable level (92.5%) at 30 kGy. No significant change of gel content (%) was observed above 30 kGy.

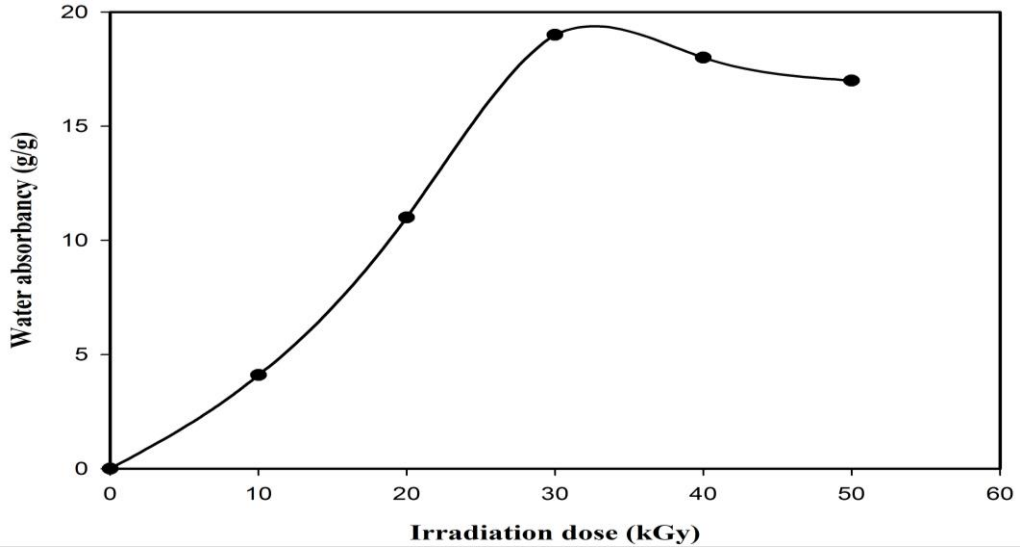

Fig. 1 Effect of irradiation dose on water absorbency of PVP/AA (1/2) hydrogel

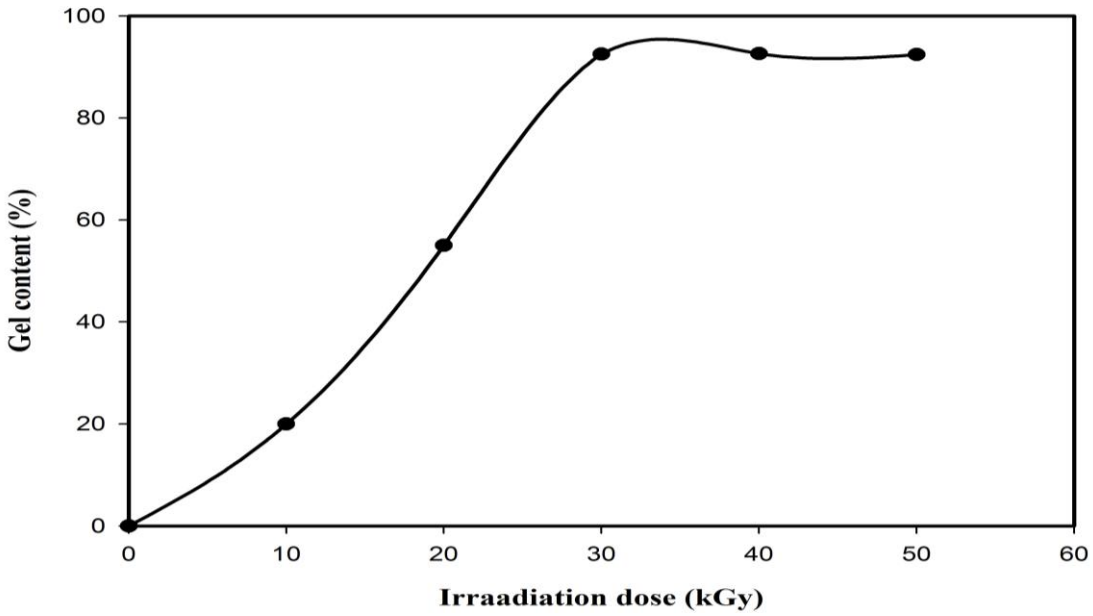

Fig. 2 Effect of the irradiation dose on the gel content of irradiated PVP/Aba (1/2) hydrogel.

3.3. Characterizations of PVA-AA hydrogel

3.3.1. X- ray diffraction

The X- ray diffraction method was used to identify the distribution and homogeneity between PVP and abeitic acid (AA) at different absorbed doses of gamma radiation. Fig.3 shows the X- ray diffraction of PVP and AA at 0, 10, 30, and 50 kGy of gamma

radiation. It can be seen that the PVP has a well definite intense and sharp diffraction peaks at 2Θ values of 11.5, 10.72, and 21.16. Also, the AA has a diffraction peaks at 2Θ values of 20.8, 23.68, and 26.45. In addition, the PVP/AA mixture has a sharp diffraction peaks without radiation at 2Θ values of 14.32, 15.64, and 17.22. On the other hand, after the exposure of PVP/AA mixture to different doses of gamma radiation, the diffraction peaks of mixture will transformed from crystalline and sharpness peaks to broadness peaks, indicating the distribution and homogeneity between PVP and AA at different doses. Moreover, it was found the PVP/AA mixture at dose of 30 kGy gave low intensity diffraction peak with high broadness compared with the same mixture without radiation, indicating the high diffusion and homogeneity between PVP and AA and this is due to the crosslinking process between two polymers

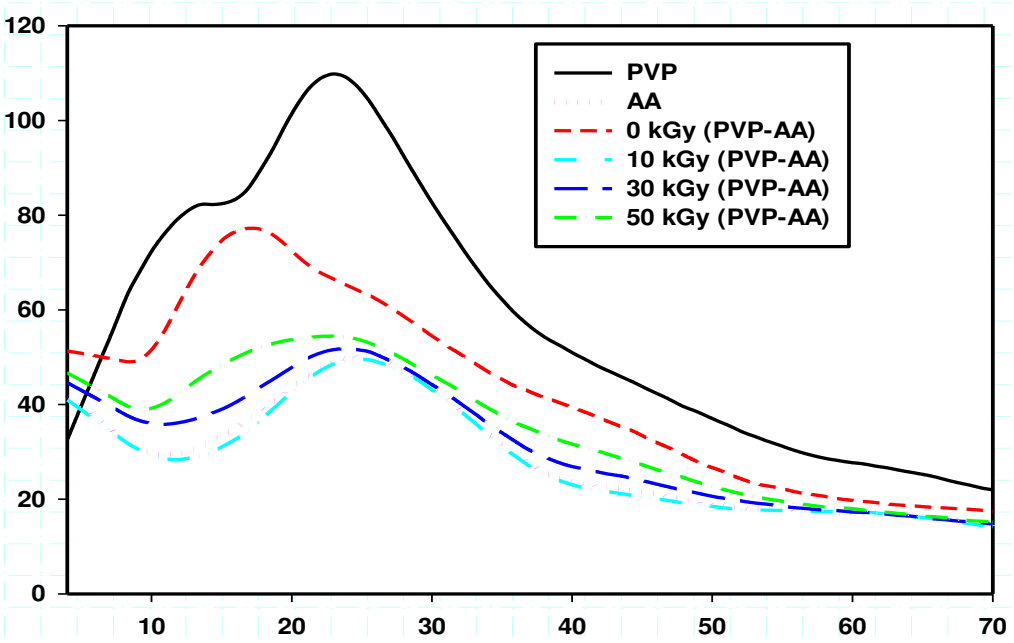

Fig. 3 X- ray diffraction of PVP and AA at 0, 10, 30 and 50 kGy of gamma radiation

3.3.2. IR- spectroscopy

It is interesting to tracking the miscibility and homogeneity between PVP and AA under different doses of gamma radiation via FTIR spectroscopy. Fig. 4 shows the FTIR spectra of PVP, AA and their blends at different doses 0, 10, 30, and 50 kGy. It can be clear from Fig.4 that the PVP has a unique peak at (3250-3550) cm^{-1} which assigned to the aliphatic amine, a sharp peak of a carbonyl group at 1646 cm^{-1}, and other strong bands at 2885 cm^{-1} and 2942 cm-1 correspond to aliphatic (C-H). On the other hand, the AA showed characteristic bands such as stretching band at (2720-

3100) cm^{-1} which corresponds to carboxylic acid, stretching band at 1690 cm^{-1} which assigned to carbonyl group, and a sharp bending band at 888 cm^{-1} due to vinyl group (=C-H). In addition to bands of aliphatic (C-H) at 2885 cm^{-1} and 2942 cm^{-1} and also stretching band of aliphatic (=C-H) at 3085 cm^{-1} [25] as seen in Fig. 2. After blending and exposure to different doses of gamma ray, it can be seen sharp bands of aliphatic (C-H) for all doses which indicate and prove the miscibility and homogeneity between PVP and AA. Also it can be seen that the stretching band of aliphatic (=C-H) was disappeared for PVP/AA blend at 10 and 30 kGy only which indicates to occurrence the crosslinking process between PVP and AA. Additionally there are a noticeable decreasing in the bending band of vinyl group (=C-H) at 10 and 30 kGy only. However the band of aliphatic (=C-H) and band of bending (=C-H) of vinyl group were appeared at 50 kGy which may be attributed to the degradation process between PVP and AA. In addition, the appearance of very sharp band at 1653 cm^{-1} which belong to the carbonyl group for miscible blend especially at 30 kGy. Hence the dose of 30 kGy was selected as the best dose for the miscibility and crosslink process between PVA and AA. Fig. 5, show the change in the band of the functional group (C=O) which responsible for the adsorption of Co, Ni, Zn and Mn on the PVP/AA adsorbent surface.

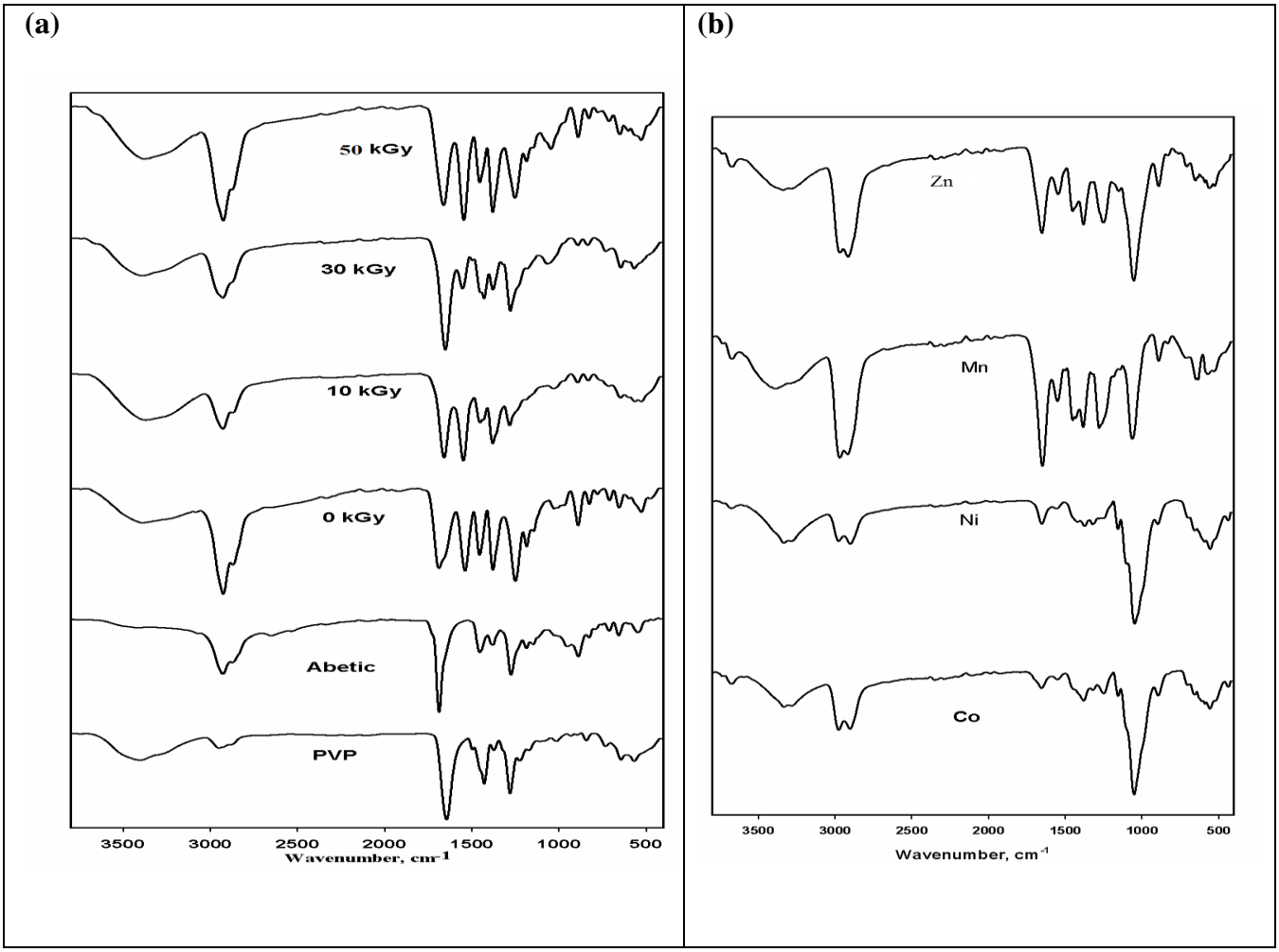

Fig. 4 (a) FTIR spectra of PVP, AA and PVP-AA at different doses 0, 10, 30, and 50 kGy.

(b) FT-IR spectra of PVP-AA after adsorption of Co, Ni, Mn and Zn from aqueous solution at radiation dose=30 kGy, V/m=0.05 L/g and pH=3.

3.3.4. Scanning electron microscopy (SEM)

Figure 6(a) to (h) shows the SEM images of PVP, AA, both un-irradiated and irradiated PVP/AA hydrogel and irradiated PVP/AA hydrogel after recovery metals (Co, Ni, Mn and Zn). The SEM pattern of PVP is shown in Figure 6(a). The surface of PVP smooth and no sign of porous structure are visible in the sample. In Figure 6(b), the SEM of the AA observed that the surface was rock shape, rough, and with sharp edges. Un-irradiated polymeric blend containing Aba/E PVP/AA shows rough surface, holes, and with a few elongated shapes. The PVP particles dispersion shows that a small interfacial tension exists between AA particles. Pore sizes of the crosslinking hydrogel of PAAm are clearly observed, and both images of SEM are

approximately similar compared to PAAm. The cavities, small holes and a network of canals have appeared between the networks of the PVP/AA at 30 kGy appear to absorb the water, but there are no cavities in the un-irradiated PVP/AA.

The image of the PVP/AA hydrogel at 30 kGy shows a more homogenous structure compared to the un-irradiated sample. Irradiation changes the polymer network; therefore, it changes the morphological state of the polymer. The radiation dose of gamma irradiation leads to an increase in cross-linking degree in the amorphous area and leads to increased molecular weight.

The changes in surface morphology were observed after uptake of metals (Co, Ni, Mn and Zn) on the PVP: AA (radiation dose=30 kGy, pH=3) as shows in Figure 6 (e) to (h). The surface became tougher and show that the holes and a network of canals have disappeared due to agglomeration of metals ions. In addition, the results of EDX mapping Fig.7 (a-d), showed that the PVP: AA could better adsorb the investigated metal ions which are in accord with the experimental results and the maximum adsorption capacity for each element.

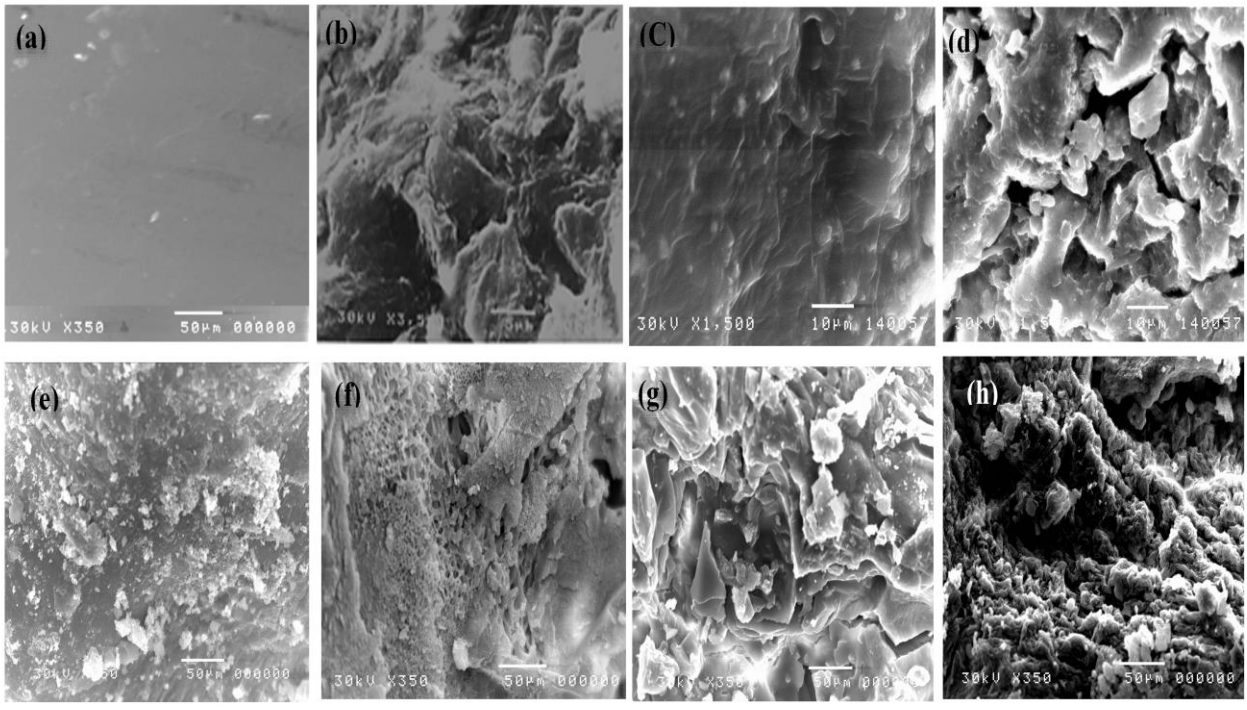

Fig. 6 SEM photographs of (a) PVP, (b) AA, (c) unirradiated PVP/AA, (d) irradiated PVP/AA at 30 kGy, (e) irradiated PVP/AA at 30 kG after adsorption of Co, (f) irradiated PVP/AA at 30 kGy after adsorption of Ni (g) irradiated PVP/AA at 30 kGy after adsorption of Mn and (h) irradiated PVP/AA at 30 kGy after adsorption of Zn

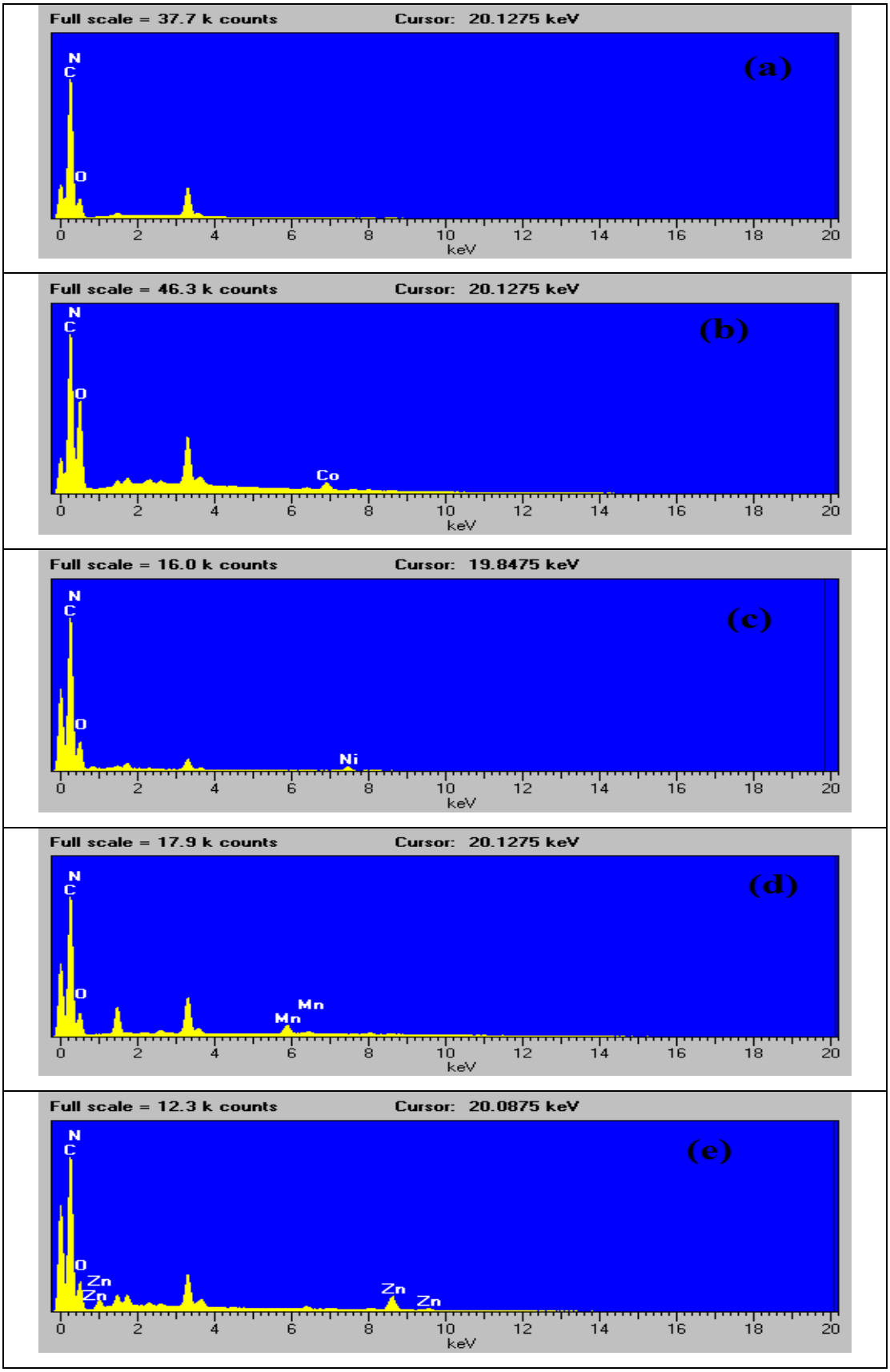

Fig. 7 EDX-analysis of (a) irradiated PVP/AA at 30 kGy (b) irradiated PVP/AA/Co (c) irradiated PVP/AA/Ni (d) irradiated PVP/AA/Mn (e) irradiated PVP/AA/Zn.

3.4. Batch Experiments of the adsorption of Zn, Co, Ni and Mn on the irradiated PVP-AA hydrogel adsorbent

The preliminary investigations on the sorption time for the recovery of Co(II), Ni(II), Zn(II) and Mn(II) metal ions from aqueous solution using the irradiated PVP-AA composite was carried out by mixing 5 mL of 100 $mg.L^{-1}$ aqueous solution of investigated metal ions with 0.1 g of the prepared adsorbent and shaken for 30 to 150 minutes at room temperature. According to the experimental results 45 is maintained as equilibrium shaking time for all investigated metal ions in all batch experiments. Different parameters such as blending ratio of PVP: AA, radiation dose, pH of the aqueous phase solution, metal ions concentrations, and temperature were optimized.

3.4.1. Sorption capacity of different blending ratio of PVP: AA composite

The adsorption of 100 $mg.L^{-1}$ of aqueous solution of the investigated metal ions under same used experimental conditions (V/m= 0.05 L/g, shaking time=45) using different blending ratio of PVP: AA at 1:1, 2:1, 9:1 and 1:2 which irradiated at 30 kGy radiation dose. The experimental results given in table (1) indicate that PVP:AA composite ratio of 1:2 give high uptake efficiency of 75%, 93.6%, 94% and 56% for Zn, Ni, Co and Mn, Fig. 8, respectively.

Table 1 Uptake efficiency of PVP: AA blend with different combination percent at radiation dose=30 kGy for the recovery of Zn, Co, Ni and Mn from aqueous solution at V/m=0.05 L/g.

Blend ratio (PVP:PVA)	**Uptake%**				**Ordering uptake Feasibility**
	Zn	**Ni**	**Co**	**Mn**	
1:1	38	34	86	56	Co>Mn>Zn>Ni
2:1	28	5	52	90	Mn>Co>Zn>Ni
9:1	16.6	9	5	52	Mn>Zn>Ni>Co
1:2	75	93.6	94	80	Co>Ni>Zn>Mn

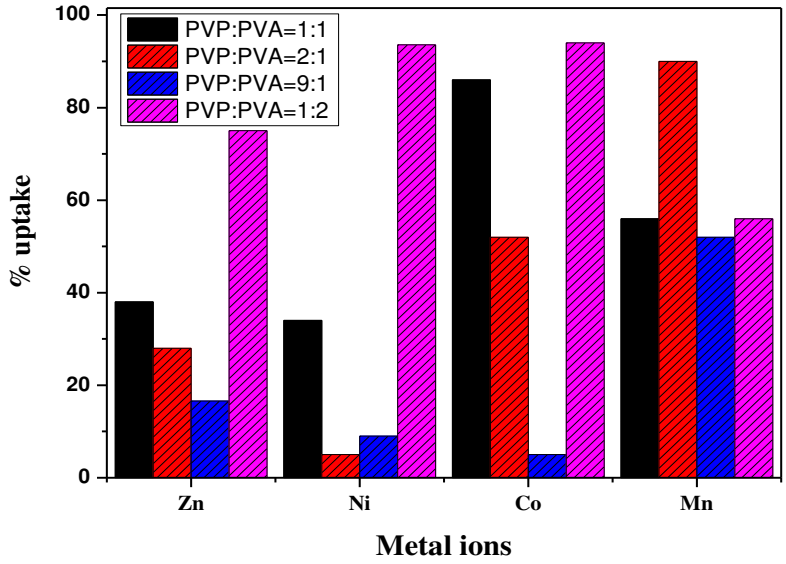

Fig. 8 Uptake efficiency of PVP: AA hydrogel blend with different combination percent for the recovery of Zn, Co, Ni and Mn from aqueous solution

3.4.2. Effect of different radiation doses on uptake efficiency of PVP: PVA blend of combination percent 1:2

The selected PVP: AA hydrogel blend ratio of 1:2 which give higher uptake% of the investigated metal ions was exposure to different radiation doses from 10 to 50 kGy. Under the used experimental conditions the different irradiated blends were implanted for adsorption of 100 mg/L of the four investigated metal ions from aqueous solution. The experimental data given in Fig. 9, show that the maximum uptake efficiency was achieved with radiation dose 30 kGy and the uptake% takes the sequence: Co>Ni>Mn>Zn, table (2) and this may be attributed to higher crosslinking between PVP and AA which increased active sites of prepared hydrogel.

Table 2 Uptake efficiency of PVP: AA hydrogel blends of ratio1:2 at different radiation doses for the recovery of Zn, Ni, Co and Mn from aqueous solution at V/m=0.05 L/g.

Blend ratio (PVP:PVA)	Radiation dose (kGy)	Uptake%				Ordering uptake Feasibility
		Zn	Ni	Co	Mn	
1:2	10	55	77	90	74.5	Co> Ni >Mn>Zn
1:2	30	75	93.6	94	80	Co>Ni>Mn>Zn
1:2	50	70	85	90	56	Co> Ni >Mn>Zn

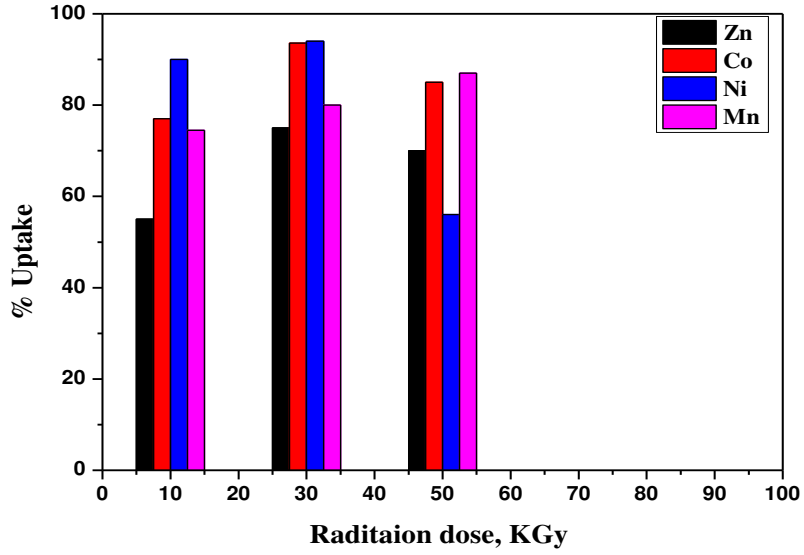

Fig. 9 Uptake efficiency of PVP: AA composite of ratio1:2 at different radiation doses for the recovery of Zn, Ni, Co and Mn from aqueous solution at V/m=0.05 L/g.

3.4.3. The effect of pH

The influence aqueous solution pH on uptake efficiency on the PVP-AA hydrogel for the recovery of 100 mg/L Zn, Ni, Co and Mn from aqueous solution was carried out in the pH range 0.75 to 8 which was adjusted by diluted nitric acid and sodium hydroxide under the used experimental conditions (radiation dose= 30 kGy,

V/m=0.05 L/g, contact time=45 min). Plotting of pH against uptake %, Fig. 10 showed that the uptake % increased gradually with increasing pH from 0.75 to 3 and further increases in pH the adsorption efficiency still constant. This is may be attributed to the protonation of adsorbent sites that decrease the adsorption of metal ions [26]. Furthermore, the reported results indicate that the favorable pH=3 which achieved high uptake efficiency with ordering sorption feasibility: Ni>Co>Mn>Zn, so that the recovery of investigated heavy metal ions was proceed from acidic aqueous solution of pH =3.

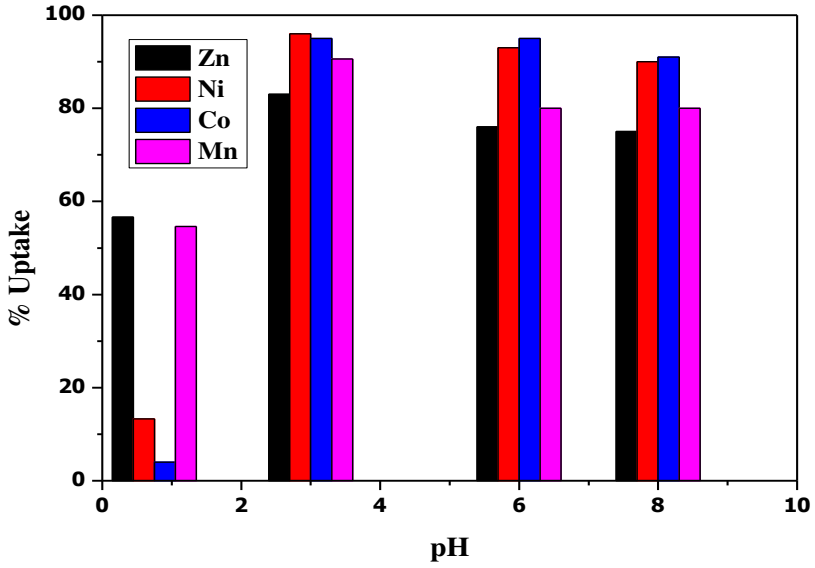

Fig. 10 Effect of pH on the recovery of Zn, Co, Ni and Mn using PVP: AA hydrogel from aqueous solution at radiation dose=30 kGy and V/m=0.05 L/g.

3.4.4. Effect of initial Zn(II), Co(III), Ni (III) and Mn(II) Concentration

The adsorption of Zn(II), Co(III), Ni (III) and Mn(II) ions using the developed PVP:AA adsorbent was investigated in concentration range 100-1000 mg/L by shaking 5 mL of the aqueous acidic solution (pH =3 and V/m=0.05 L/g, radiation dose=30 kGy) individually and were shaken for 45 min at room temperature. According to Fig. 11, the adsorption uptake efficiency decrease as initial metal ion concentration increases with maximum adsorption capacity reached 32, 32.5, 19.5 and 31 $mg.g^{-1}$ for Zn(II), Co(III), Ni (III) and Mn(II) ions respectively. This behavior may

be attributed to the interactions between the active sites of PVP:AA hydrogel adsorbent and the investigated metal ions.

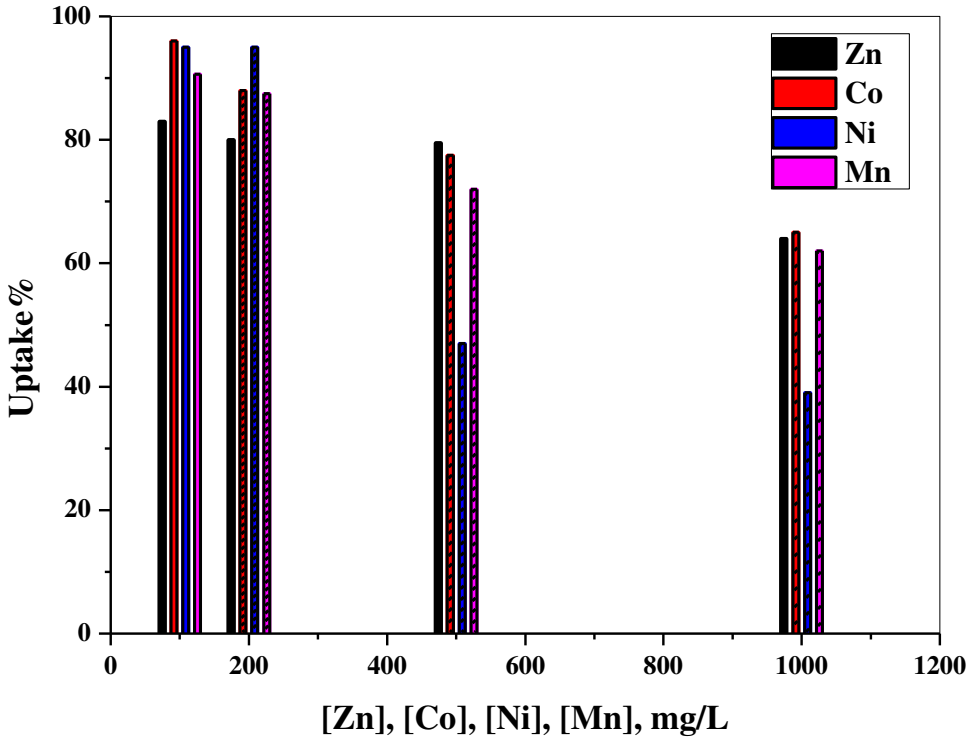

Fig. 11 Effect of different metal ions concentrations on the sorption of Zn (II), Co(II), Ni(II) and Mn(II)from acidic nitrite solution at radiation dose=30 kGy, V/m=0.05 L/g and pH=3.

3.4.5. Influence of temperature

The influence of temperature was studied by mixing 5 ml of 100 mg/L Zn, Co, Ni and Mn from aqueous acidic solution (pH=3) individually with 0.1 g of PVP:AA adsorbent and were shake at different temperatures (15-45 ^{o}C) for 45 min. Fig.12, illustrate that, with the increasing of temperature, the uptake% of adsorbent increased slightly in the case of Zn, Co(II), Ni. This is may be due to the increase in the number of the active sites of the adsorbent at the elevated temperature which will increase and enhance the adsorption capacity of the investigated ions. But in case of Mn(VI) the uptake% decreased sharply from 92% to 72% this due to increasing collision between manganese ions, which decrease the chance of interaction between adsorbent and ions.

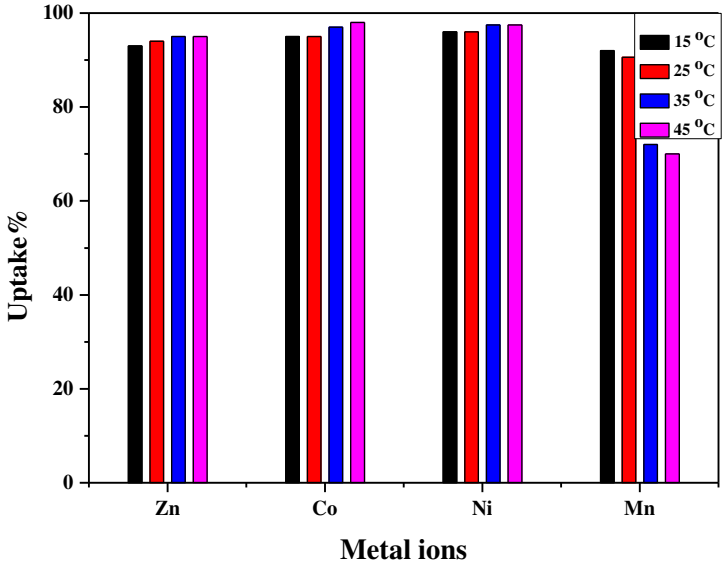

Fig.12 Effect of temperature on the sorption of Zn, Co(II), Ni and Mn on PVP-AA composite from aqueous acidic solution at radiation dose=30 kGy, V/m=0.05 L/g and pH=3.

Thermodynamic parameters (ΔG), (ΔH) and (ΔS) were calculated under different investigated temperatures using the following equations [24]:

$$\log K_d = \frac{\Delta H}{2.303R}\ \frac{1}{T} + \frac{\Delta S}{R} \qquad (6)$$

$$K_d = \frac{(C_i - C_e)}{C_e} \qquad (7)$$

$$\Delta G = \Delta H - T\,\Delta S \qquad (8)$$

Where R is the universal gas constant (8.314 J $mol^{-1}K^{-1}$) and T is the absolute temperature in Kelvin (K).Where K_d is the distribution coefficient. Fig. 13, Illustrate the plot of $\log K_d$ versus 1/T in which the values of ΔH and ΔS can be calculated from the slope and intercept that were tabulated in table (3).

The experimental results indicate that the positive values of ΔH and ΔS for Zn, Co and Ni show endothermic nature and the increasing randomness at the interface between the adsorbent and the aqueous phase during the adsorption processes. Otherwise, the negative values of ΔG confirm that the adsorption process of Zn, Co and Ni on the PVP-AA adsorbent is non-spontaneous process. On the Other hand, the negative values of ΔH, ΔG and ΔS for Mn (II) indicating that the adsorption system of

PVP/AA/Mn has exothermic and non-spontaneous nature with decreasing the randomness during the adsorption process.

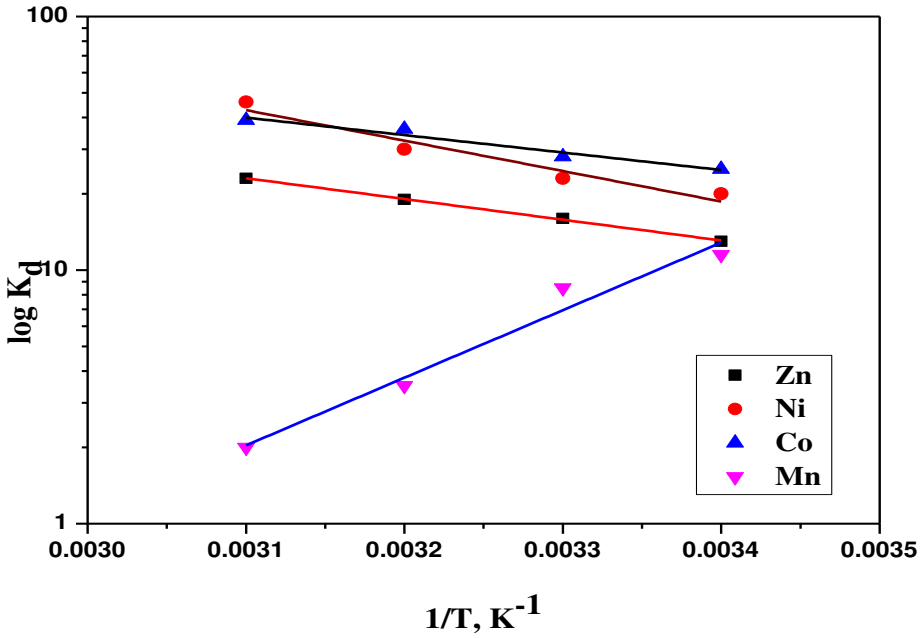

Fig. 13 The relation between of logK_d vs 1/T for the adsorption of Zn, Co, Ni and Mn using PVP-AA at radiation dose=30 kGy, V/m=0.05 L/g and pH=3.

Table 3 Thermodynamic parameters for the adsorption of Zn, Co(II), Ni and Mn on PVP-AA hydrogel from aqueous solution.

Metal ion	Slope	Intercept	ΔH ($kJmol^{-1}$)	ΔG ($kJ\ mol^{-1}$)	ΔS ($KJmol^{-1}$)	R^2
Zn(II)	-817.5	3.9	15.7	-6.8	75.5	0.998
Co(II)	-1200.5	5.35	23.3	-7.4	102	0.975
Ni(II)	-668.5	3.73	13.2	-8.2	71.8	0.980
Mn(II)	2664	-7.1	-51	-5.6	-45.4	0.983

3.5. Desorption and Regeneration investigation

The investigations of desorption procedures was carried out by loaded 100 mg/L of Zn, Co, Ni and Mn on PVP-AA hydrogel adsorbent using different desorption agents such as distilled water, nitric acid, sodium sulfate and oxalic acid at radiation dose =30 kGy, V/m=0.05 L/g and pH=3 to find a suitable desorption agent. The desorption efficiency (D %) was estimated using the subsequent equation [27] :

$$D\% = \frac{(C_a - C_d)}{C_a} \qquad (9)$$

Where C_a and C_d are the concentration of ions adsorbed and desorbed (mg/L), The tabulated data in table (4) show that maximum stripping efficiency for Co, Ni of 99% was achieved with 1 M nitric acid (2 stages), as well as 99% and 35% for Mn and Zn were achieved with 5 M oxalic acid (3 stages). On other hand the regenerated PVP-AA adsorbent (using nitric and oxalic acids) was implanted to second sorption process with the same batch optimum conditions (PVP-AA at radiation dose=30 kGy, V/m=0.05 L/g and pH=3, contact time=45 min). The results of reusability indicate that the regenerated PVP-AA was reused for three sorption cycles with uptake efficiency of 45%, 60%, 60% and 70% for Zn (II), Co(II), Ni(II) and Mn(II) respectively, which show the high performance and repeatability of PVP-AA sorbent for the recovery and removal of heavy metal ion from aqueous solution.

Table 4 Desorption of Zn, Co, Ni and Mn with different concentrations of stripping agents after adsorption with 0.1 g PVP-AA adsorbent at 25 ^{o}C.

Desorption agent	Conc. , M	Desorption % (D %)			
		Zn(II)	Co(II)	Ni(II)	Mn(II)
Distilled-H_2O (2 stages)	-	25	32	93	-
Nitric acid (2 stage)	1	20	99	99	10
Na_2SO_4 (2 stages)	0.5	20	96	-	-
Oxalic acid (3 stages)	5	35	58	75	99

3.6. Beneficiation of the prepared PVP/AA hydrogel

The most important interpretation of the experimental results obtained from the different used methods and adsorbents were compared with the prepared PVP:AA hydrogel adsorbent. Table 5 shows the comparison between different types of adsorbent materials, reported from previous work [16], [26] and [29-31] and those of the synthesized PVP:AA hydrogel sorbent. The reported results concluded that the synthesized green adsorbent has a high adsorption efficiency and capacity than other materials which makes it more sustainable for the removal and trapping of heavy metal ions such Zn, Co and Ni and Mn from aqueous solution.

Table 5 Comparison between the synthesized PVP:AA hydrogel adsorbent and other reported materials.

Adsorbent	Sorption capacity (mg/g)				References
	Zn(II)	Co(II)	Ni(II)	Mn(II)	
PVP:AA hydrogel	32	32.5	19.5	31	Current work
Amine-functionalized SBA-15	17.5	-	1.9	-	26
Jute/Polyacrylic acid hydrogel	188	96	-	17	16
kaolinite	-	0.919	1.669	0.446	29
Natural Zeolites	2.356	3.73	-	0.869	30
carbon gels	-	7	5	-	31

3.7. Conclusion

* PVP-AA hydrogel blend have been successfully prepared via gamma irradiation with 30 kGy for the potential removal of Zn, Co, Ni and manganese metal ions from acidic solution.

* The optimum adsorption pH of the investigated metal ions aqueous solution was found to be pH=3 and the uptake% take the sequence: Ni>Co>Mn>Zn.

* The maximum sorption capacity of PVP-AA adsorbent was found to be reached 32, 32.5, 19.5 and 31 mg/g for Zn, Co, Ni and Mn respectively.

* Desorption investigation show that the maximum stripping of the adsorbed investigated metal ions was achieved with 1 M nitric acid and take the order: Co>Ni>Zn>Mn.

* The obtained results indicate that PVP-AA hydrogel is a promising adsorbent for the application in the recovery and separation process of heavy metal ions from acidic solution.

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Figures

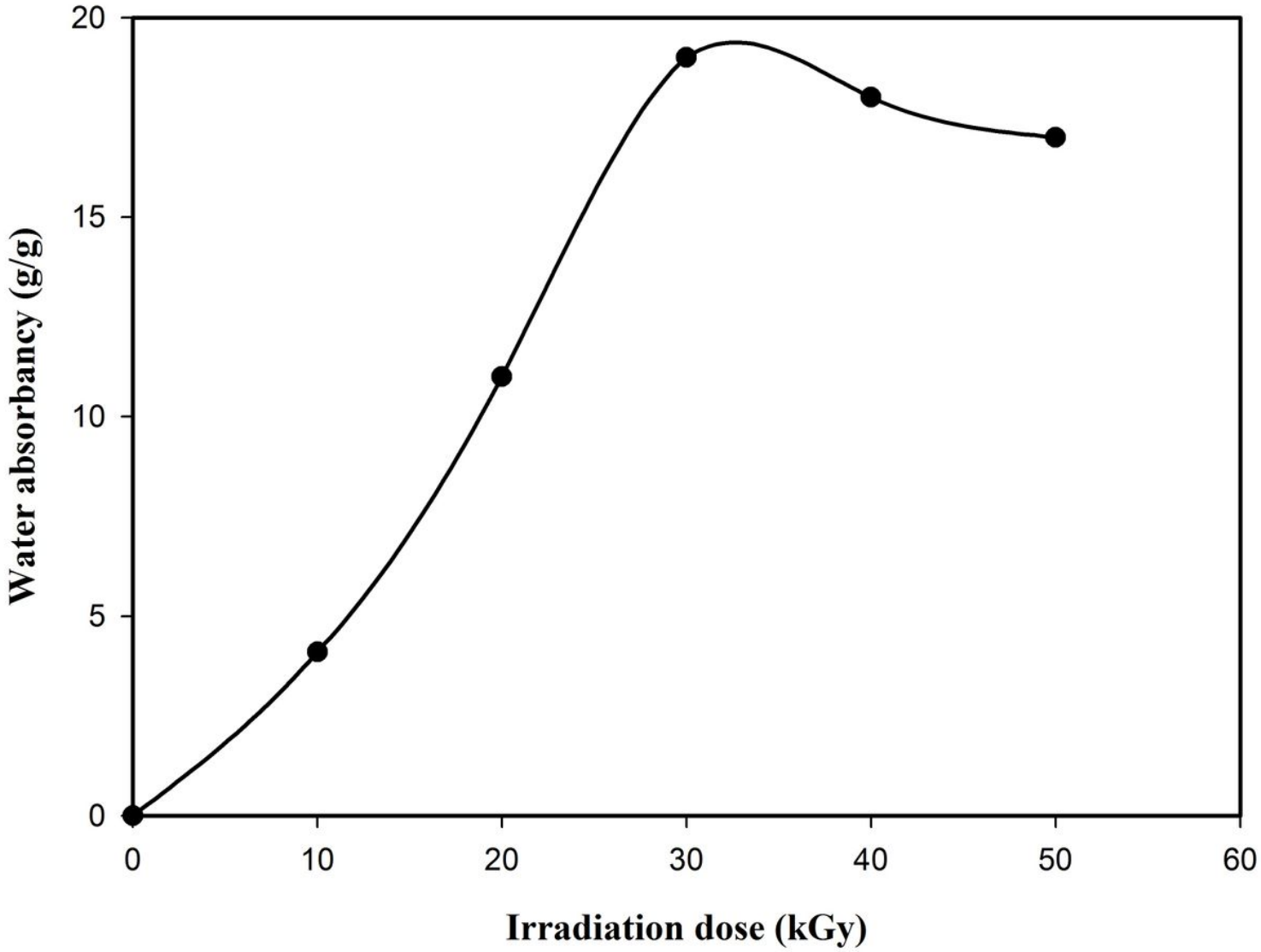

Figure 1

Effect of irradiation dose on water absorbency of PVP/AA (1/2) hydrogel

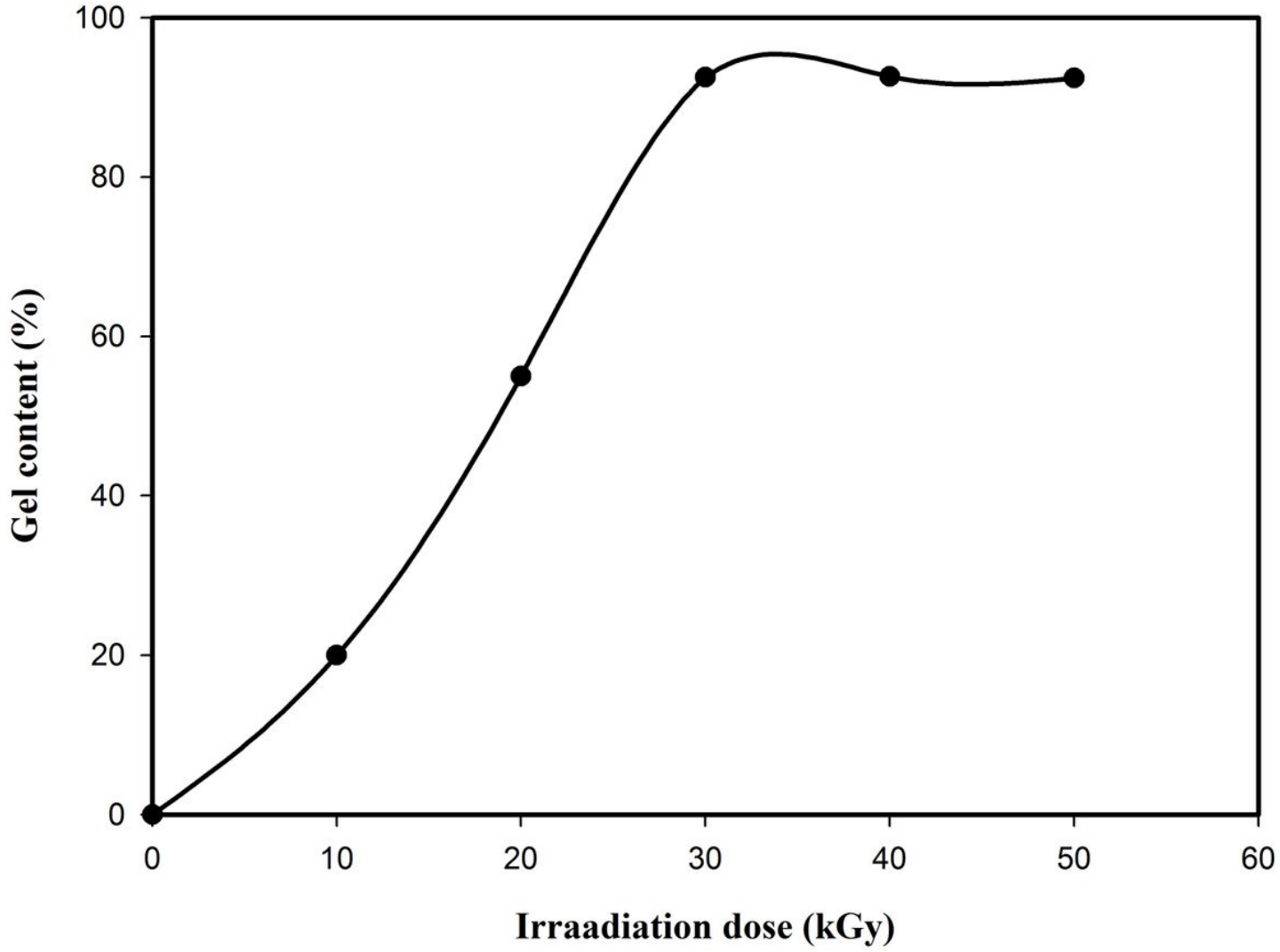

Figure 2

Effect of the irradiation dose on the gel content of irradiated PVP/Aba (1/2) hydrogel.

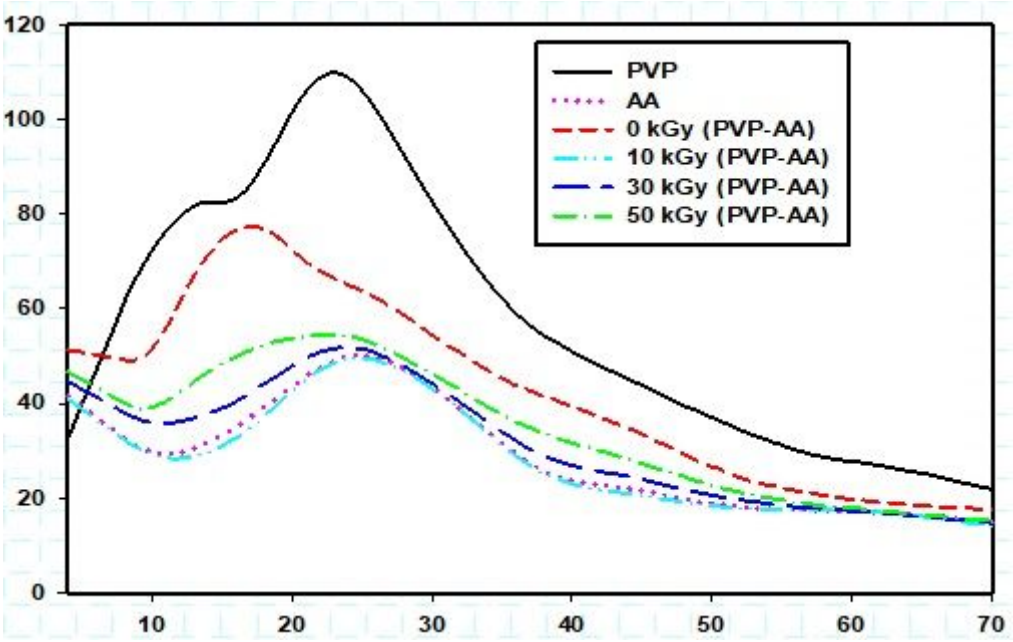

Figure 3

X- ray diffraction of PVP and AA at 0, 10, 30 and 50 kGy of gamma radiation

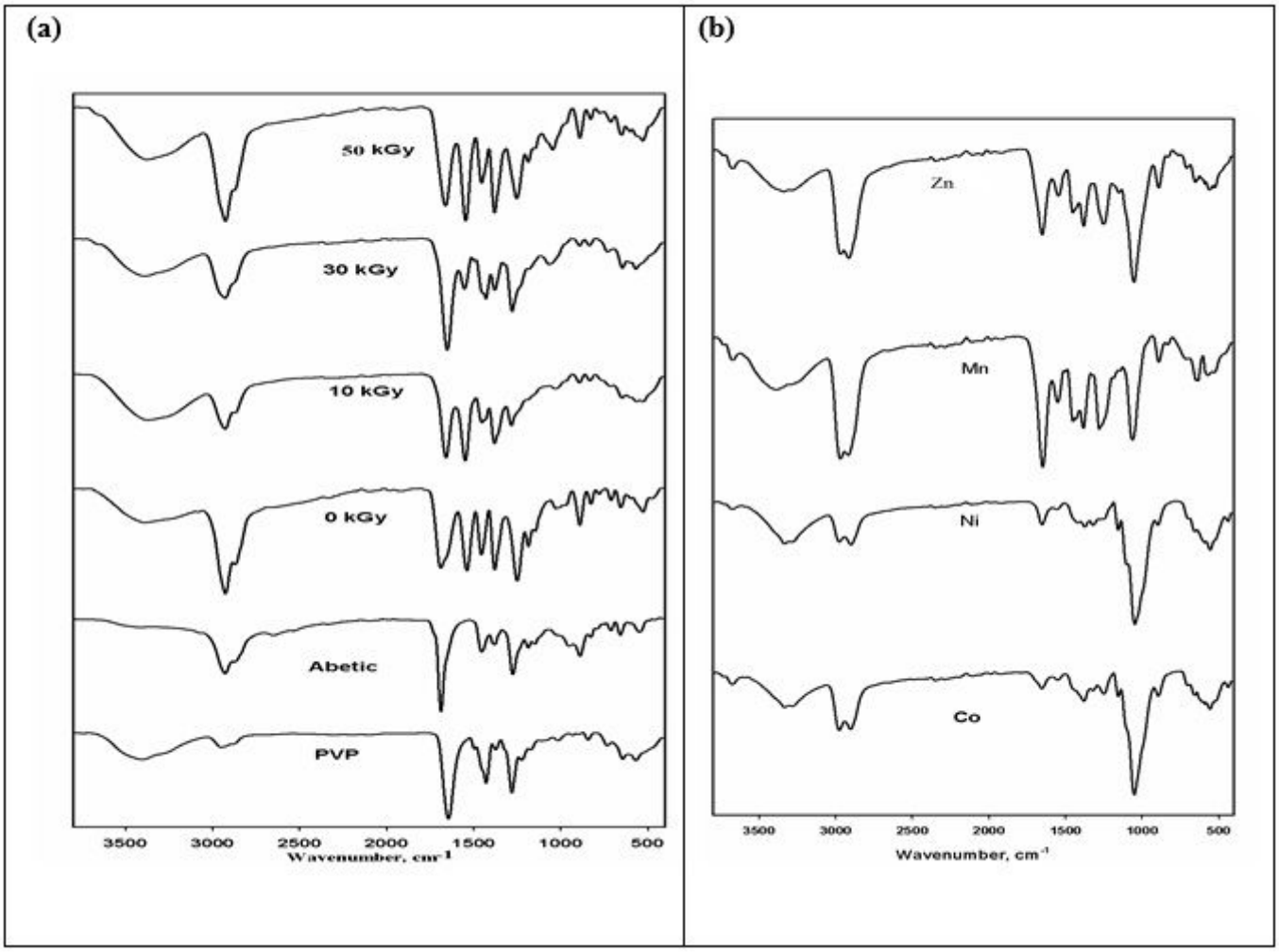

Figure 4

(a) FTIR spectra of PVP, AA and PVP-AA at different doses 0, 10, 30, and 50 kGy. (b) FT-IR spectra of PVP-AA after adsorption of Co, Ni, Mn and Zn from aqueous solution at radiation dose=30 kGy, V/m=0.05 L/g and pH=3.

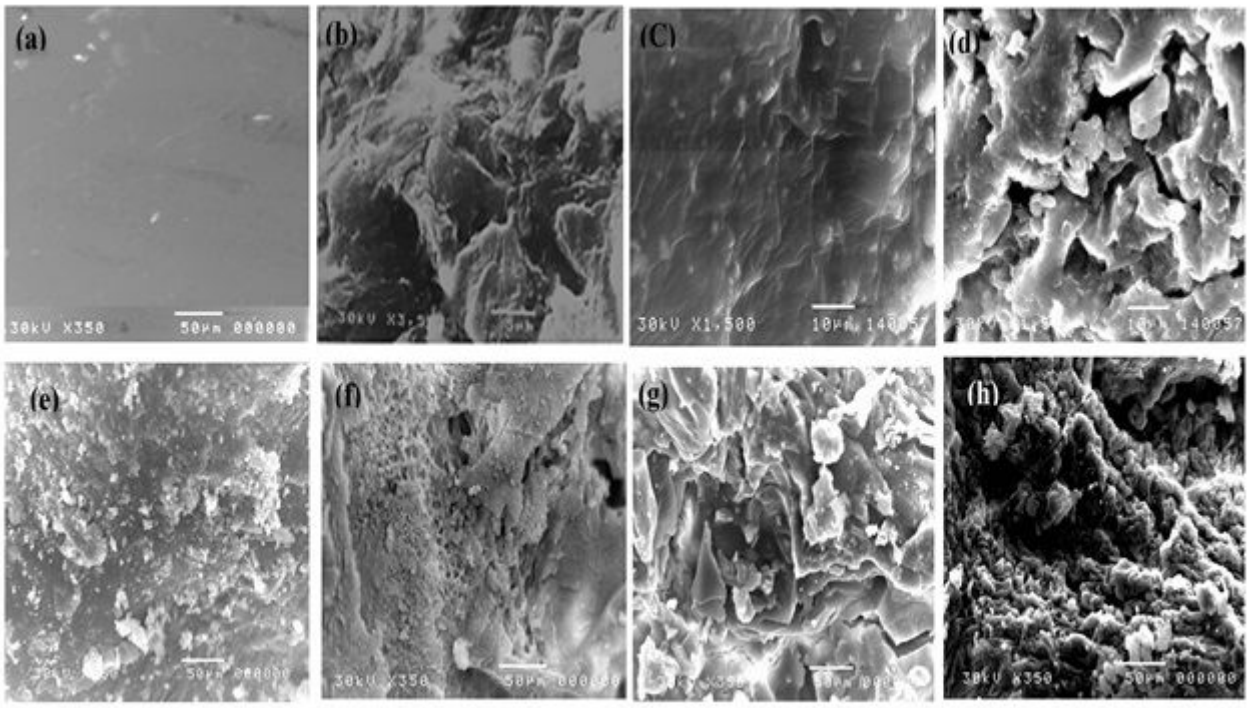

Figure 5

SEM photographs of (a) PVP, (b) AA, (c) unirradiated PVP/AA, (d) irradiated PVP/AA at 30 kGy, (e) irradiated PVP/AA at 30 kG after adsorption of Co, (f) irradiated PVP/AA at 30 kGy after adsorption of Ni (g) irradiated PVP/AA at 30 kGy after adsorption of Mn and (h) irradiated PVP/AA at 30 kGy after adsorption of Zn

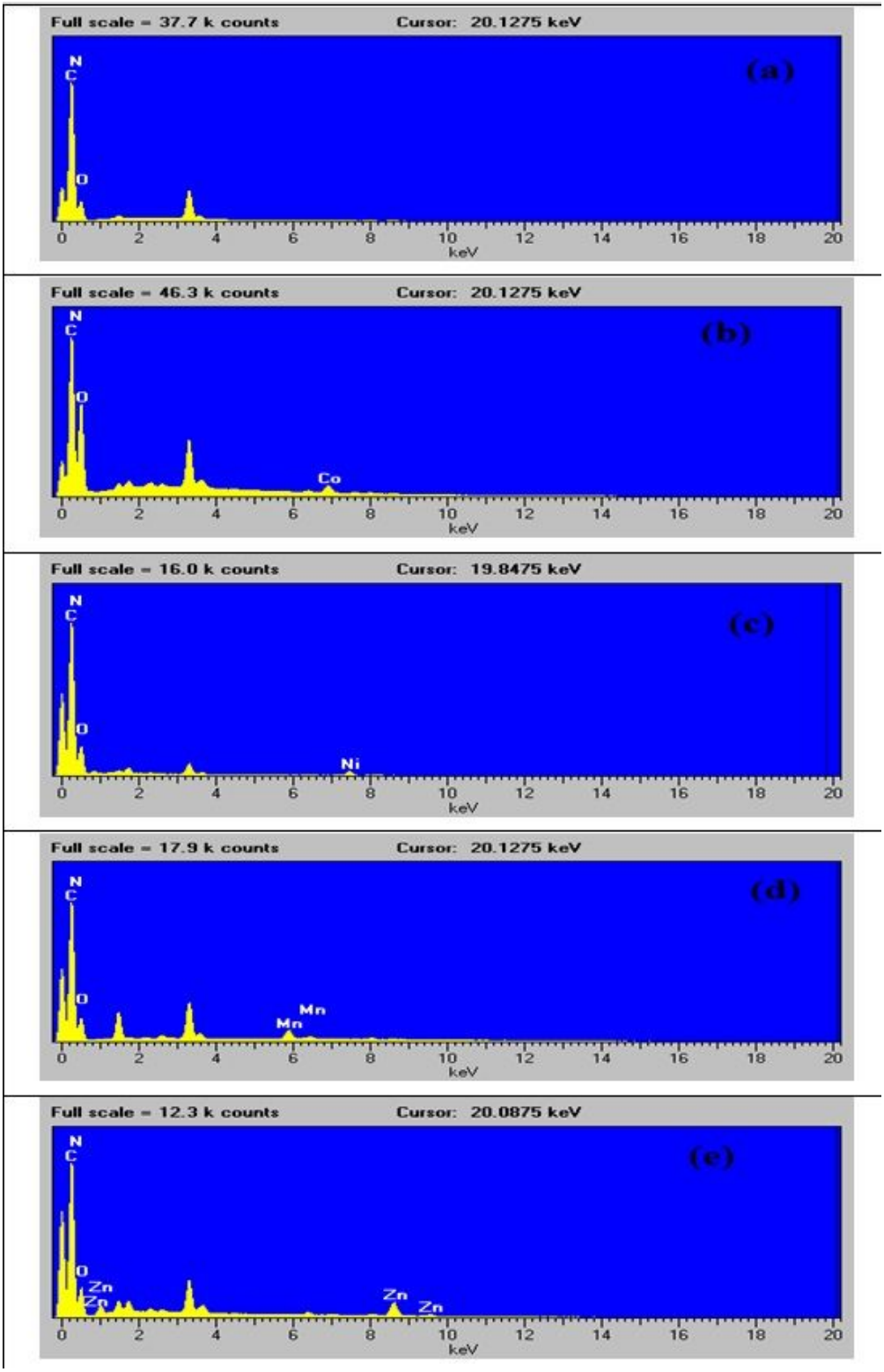

Figure 6

EDX-analysis of (a) irradiated PVP/AA at 30 kGy (b) irradiated PVP/AA/Co (c) irradiated PVP/AA/Ni (d) irradiated PVP/AA/Mn (e) irradiated PVP/AA/Zn.

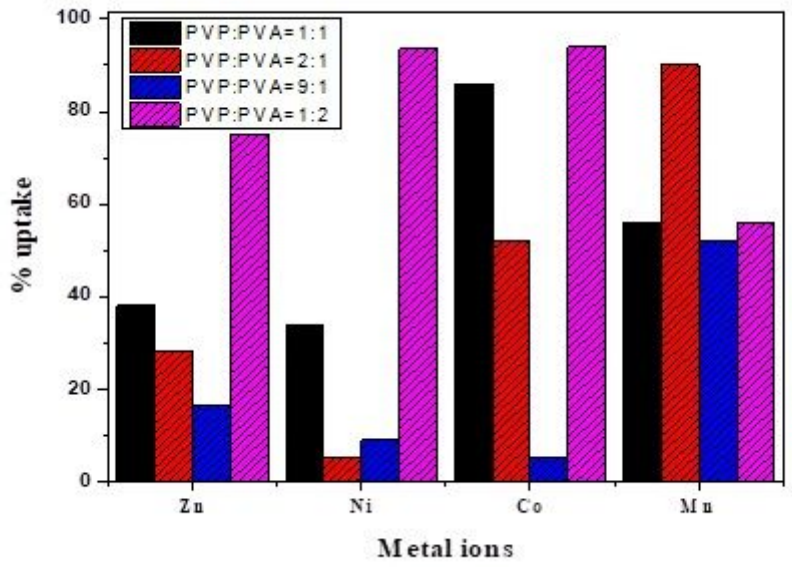

Figure 7

Uptake efficiency of PVP: AA hydrogel blend with different combination percent for the recovery of Zn, Co, Ni and Mn from aqueous solution

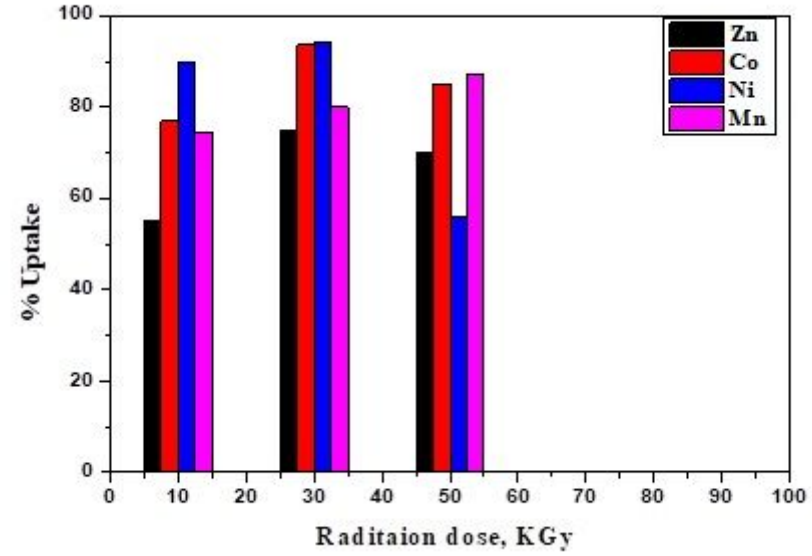

Figure 8

Uptake efficiency of PVP: AA composite of ratio1:2 at different radiation doses for the recovery of Zn, Ni, Co and Mn from aqueous solution at V/m=0.05 L/g.

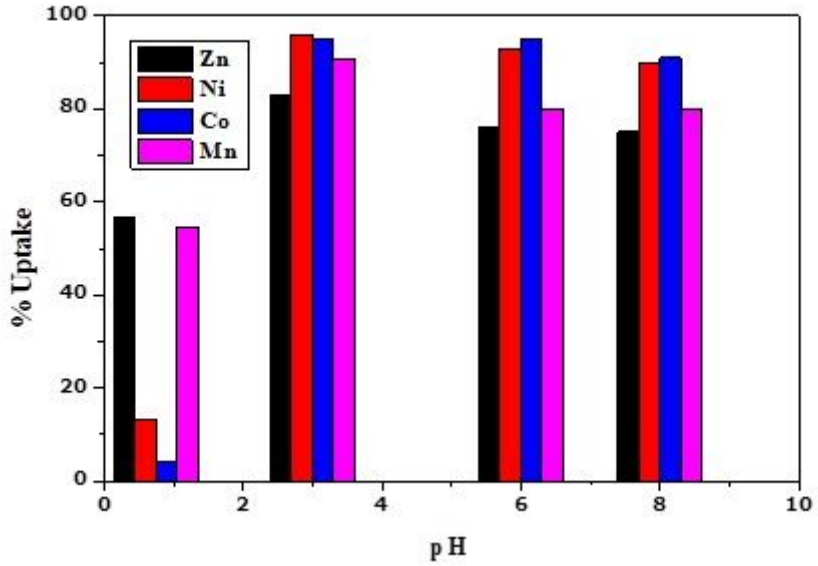

Figure 9

Effect of pH on the recovery of Zn, Co, Ni and Mn using PVP: AA hydrogel from aqueous solution at radiation dose=30 kGy and V/m=0.05 L/g.

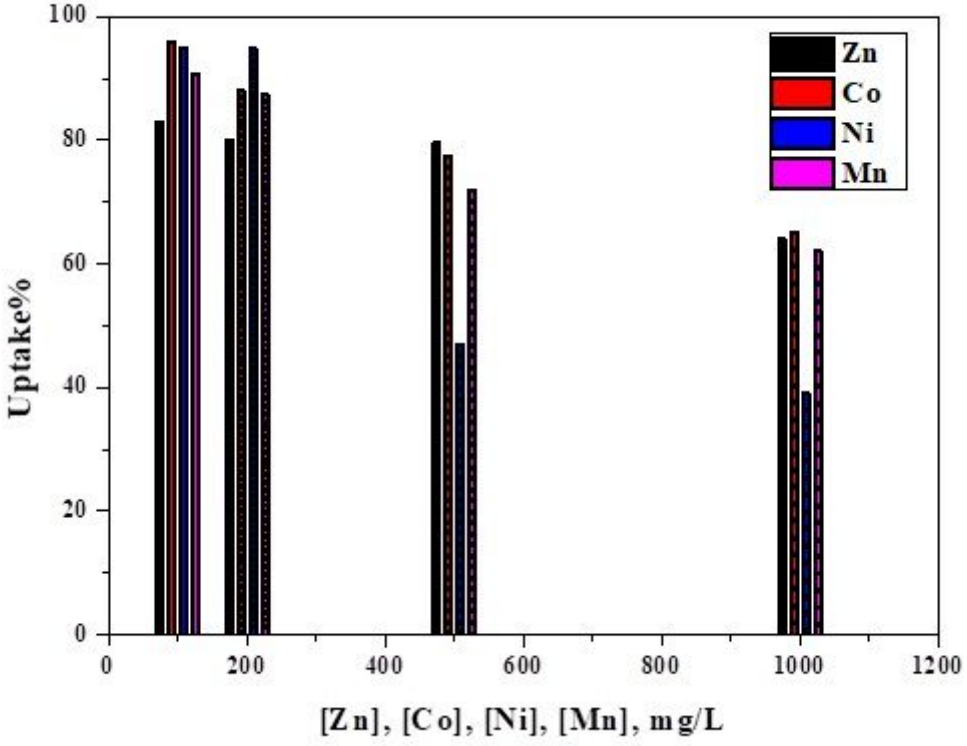

Figure 10

Effect of different metal ions concentrations on the sorption of Zn (II), Co(II), Ni(II) and Mn(II)from acidic nitrite solution at radiation dose=30 kGy, V/m=0.05 L/g and pH=3.

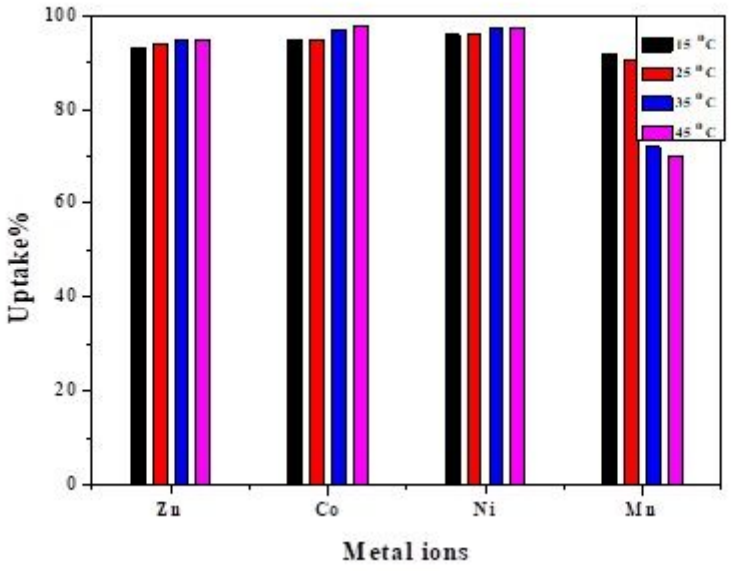

Figure 11

Effect of temperature on the sorption of Zn, Co(II), Ni and Mn on PVP-AA composite from aqueous acidic solution at radiation dose=30 kGy, V/m=0.05 L/g and pH=3.

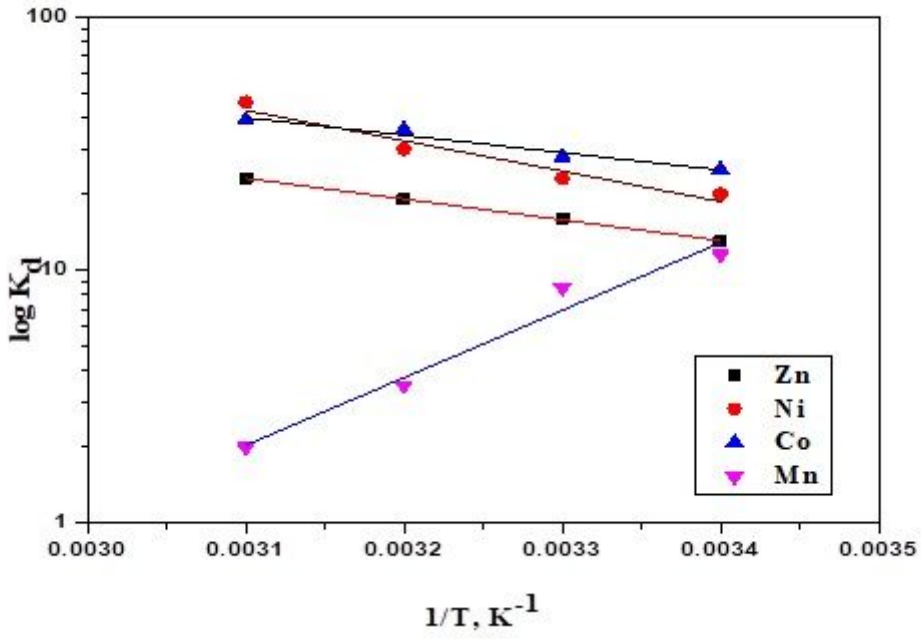

Figure 12

The relation between of logKd vs 1/T for the adsorption of Zn, Co, Ni and Mn using PVP-AA at radiation dose=30 kGy, V/m=0.05 L/g and pH=3.

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