



Preparation of Pectin–Acrylamide–(Vinyl phosphonic acid) hydrogel and its selective adsorption of metal ions

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Abstract

Selective metal adsorption is a prominent and novel field in adsorption science where functional hydrogels are playing vital roles. The current study is mainly focused on the synthesis of Pectin–Acrylamide–Vinyl phosphonic acid hydrogels (Pectin–AAM–VPA) and the selective adsorption of metal ions from the solution of multielement. The hydrogels were prepared by applying gamma radiation of different doses ranging from 5 to 50 kGy where 20 kGy was optimized based on the gel content and the equilibrium swelling analysis. The functional groups of the hydrogel were identified by FTIR spectroscopic analysis. Thermal properties—glass transition and melting temperature of the gel were investigated by DSC thermogram. It was an amazing finding that the hydrogels show selective adsorption toward Al, Fe, Ga, In, Mo, and Bi metal ions from the solution containing 27 metal ions. The surface of the gels before and after metal adsorption was inspected using SEM supported by EDS and confirmed the selective adsorption. Metal ions were desorbed successfully in 5% nitric acid. Finally, it can be stated that the Pectin–AAM–VPA hydrogels can effectively be used for selective adsorption of Al, Fe, Ga, In, Mo, and Bi metal ions from the multielement solutions.

Keywords Pectin · Hydrogel · Selective adsorption · Gamma radiation · Multielement

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Introduction

Selective metal adsorption means the adsorption of a metal ion or a group of metal ions from a multielement solution using an appropriate adsorbent [1]. Metal toxicity in the environment is increasing in parallel with the growing industry, use of material substances, and random disposal of goods containing metallic components [2]. The metals which affect the human body, animals, and plants in different doses and forms are referred to as toxic metals. Different toxic metals affect the environment and living organisms in various ways resulting in the disturbance of the ecosystem [3, 4]. Consequently, pollution control by removing or recycling toxic metals is becoming a burning issue globally. But, most adsorption researchers focus on the adsorption of metal from solutions containing one or two to five metals which is a common but not so an effective procedure [5]. However, because each metal has different environmental impacts and economical demands, has led to the establishment of a new agenda of working on selective metal adsorption. In recent years, a few researchers are working on selective metal adsorption/removal from the sea/waste-water. Taewook Kang et al. did an appreciable work on the selective adsorption of Pt^{2+} and Pd^{2+} over Ni^{2+} , Cu^{2+} and Cd^{2+} by using thiol functionalized mesoporous silica where the selectivity was examined within five metals [6]. Rumi chand et al. used porous carbon for selective adsorption of gold-Au(III) over Pt (IV), Pd(II), and Cu(II) and Fe(III), Ni(II) metals and found good results too [7]. Xinqing Chen et al. recovered gold by adsorbing on silk Sericin and chitosan bio-sorbents which are low-cost adsorbents. Hence, the experiment was performed using groups of two, five, and six metals separately and found gold selectivity in all cases [8]. All of the above researches are confined to between two to six metal solutions from which one metal was separated selectively. There are a lot of substances/adsorbents for the recovery/recycling of metals from sea/waste-water worldwide. Among them, hydrogels are becoming dominant candidates for their super-absorbency, biodegradability, and reusability. Hydrogels are three-dimensional polymeric networks capable of holding a large amount of water/solvent in their structure without dissolving [9]. Owing to the presence of functional groups such as carboxylic acid ($-\text{COOH}$), hydroxyl ($-\text{OH}$), amide ($-\text{CO}-\text{NH}_2$), and sulfonic acid ($-\text{SO}_3\text{H}$). The hydrogels can retain water/solvent and are able to show good adsorption performance [10]. Hydrogels can be prepared by grafting natural polymer with monomers having functional groups which exhibit selective adsorption to specific metals or groups of metals or dyes [11]. Between chemical and radiation methods of hydrogel preparation, the later one is more preferable because of its simplicity, time-saving and pure yielding. Moreover, the radiation method does not need to use cross-linking agents or initiators for the reaction to proceed [12]. By applying gamma radiation, the synthesis of various hydrogels reported previously where Starch based [13], Pectin based [14], Cellulose based [15], Chitosan based [16], double network [17] and conductive hydrogels [18] is mostly significant.

Among the natural polymers, pectin is the most available, biodegradable, water-soluble, easily undergoes hydrogel formation and contains hydroxyl,

carboxyl, and ester groups in its structure resulting in higher water absorbency. Acrylamide (AAm) is the precursor of many hydrogel syntheses because it increases the swelling and can act as a linker between two polymers [19]. Vinyl phosphonic acid is a simple derivative of carboxylic acid and shows various interesting properties especially, due to the presence of the phosphonic acid group, and can be used to produce copolymer with acrylic acid, acrylamide, acrylonitrile, *N*-isopropyl acrylamide, vinylpyrrolidine, and methacrylic acid [20, 21]. Vinyl phosphonic acid (VPA) possesses a vinyl (double bond) group in its structure which can undergo copolymerization with other monomers or polymers like pectin. Katsuhiko Nakamae et al. reported the stimuli responsive swelling of phosphate group containing hydrogels insisting the preparation of phosphonic acid-based hydrogel [22]. The phosphonic acid part of the monomer can be acted as an adsorbing functional group on the surface of hydrogel [23, 24]. There are different types of hydrogels for using in various fields of study. However, gamma radiation-induced Pectin–VPA-based hydrogels for selectively metal adsorption has not been investigated yet. So, the Pectin–Vinylphosphonic acid-based hydrogel may be synthesized and used for selective adsorption of metal ions. The aim of this study is to synthesize Pectin–AAm–VPA hydrogel by applying various doses of gamma radiation and to investigate the selective adsorption toward specific metal or group of metal ions.

Experimental

Materials reagents

Citrus pectin and acrylamide were provided by Kishida Chemical Co. Ltd. Japan. vinyl phosphonic acid (97%) and Multielement standard solution 5 (10 mg/L: Ag, Al, Ba, Be, Bi, Cd, Co, Cr, Cs, Cu, Ga, In, Li, Mg, Mn, Mo, Ni, Pb, Rb, Sr, Tl, V, Zn, and 100 mg/L: Ca, Fe, K, Na), for inductively coupled plasma-mass spectroscopy (ICP-MS) was supplied by Sigma-Aldrich, Germany. All samples were prepared using ultra-pure water and the temperature was kept at 198 K for the experiments. Different pH solutions were prepared using nitric acid (HNO₃) and ammonium hydroxide (NH₄OH).

Instruments and apparatus

Functional groups of Pectin–AAm–VPA hydrogel were analyzed by FTIR spectroscopy (JASCO FTIR 4100). Measurement of thermal properties of a pre-dried gel was taken by DSC (DSC 6300 for gel, NETZSCH, DSC 200 F3 Maia for pectin powder) under a continuous N₂ gas flow and heating rate of 5 °C/min. The surface morphology of dried hydrogels was observed with an SEM (Shimadzu Corporation—Superscan SU3500, Japan) equipped with an EDS. The concentrations of metal ions in the solution were analyzed by ICP-MS (ICP/MS, Agilent 7700× series, Japan).

Preparation of hydrogel

Gelatinized pectin solution was prepared by dissolving pectin in water at 40 °C temperature and stirring at 500 rpm. The AAm and VPA were added to make the blend. The blend solution was prepared in different ratios of raw materials to get a better yield and taken in a glass tube. Nitrogen gas was passed through the blend solution to remove other gases from the tube. Then the samples were subjected to irradiation from a Co-60 gamma source at different doses ranging from 2 to 50 kGy. The gamma radiation source is the point source where the radiation doses are dependent on the distance between the sample and gamma source, and irradiation time. After irradiation for a certain period of time (as per recommended doses) the samples were taken and observed whether the hydrogels formed or not. The samples which undergo hydrogel formation (Tables 1 and 2, Fig. 1) were then cut into small pieces and extracted in water at 40 °C temperature as well as the homo-polymer and unreacted monomers were removed. Since the 5% Pectin + 10% VPA gel is not solid, so, its extraction, swelling measurement and further processing is quite difficult.

Determination of gel fraction

The gel fraction of Pectin–AAm–VPA gels was determined by soaking dried hydrogel samples in a beaker possessing ultra-pure water at 40 °C for 24 h. The hydrogel samples were taken out and dried to a constant weight in an oven at 50 °C. The equation for calculating the gel fraction of the sample can be expressed by-

$$\text{Gel fraction } [\%] = \frac{W_1}{W_0} \times 100\% \quad (1)$$

where W_0 and W_1 are the dried-gel weights before extraction and after extraction, respectively.

Table 1 Different composition of monomers and observation after gamma irradiation

Composition of raw materials	Observation
Only 10% and 15% Vinyl Phosphonic Acid (VPA)	No hydrogel found
5% Pectin + 10% (PVA)	Very weak (not solid) gel found
5% Pectin + 10% (AAm) + 15% (VPA)	Solid hydrogel found

Table 2 Radiation dose and respective gel products for Pectin–AAm–VPA

Radiation Dose (kGy)	2	5	10	20	30	40	50
Dose Rate (Gy/h)	88	217	449	828	1231	1674	2150
Distance from the Source (cm)	44	26	16	10.5	8	6.5	5.5
Gel product	No gel	Solid gel	Solid gel	Solid gel	Solid gel	Solid gel	Solid gel

Determination of equilibrium swelling

To observe the water absorbency and to predict the adsorption of metal ions on hydrogel, the equilibrium swelling was measured at pH=3 (acidic medium) as it is the pH for adsorption experiments. The hydrogel samples were kept in water for 24 h at 25 °C temperature. The samples were taken out from the solvent, blotted with filter paper and weight measured. Another two readings at 25 and 26 h were taken to confirm that the equilibrium swelling was reached.

Then the equilibrium swelling was evaluated using the following equation-

$$\text{Water absorption [\%]} = \frac{W_t - W_1}{W_1} \times 100\% \quad (2)$$

where W_1 and W_t are the dried-gel weight and the gel weight after swelling in the water, respectively.

Selective of adsorption and desorption multielement

To investigate the selectivity of Pectin–AAM–VPA hydrogels toward specific metal or group of metal ions, 1000 ppb (1 ppm) solution was prepared by dilution of multielement standard solution 5. The multielement solution is acidic and the metal adsorption usually takes place in acidic medium [25, 26]. That is why, pH=3 was maintained at 25 °C temperature. The hydrogel samples were dried well and soaked in 100 ml solution with stirring at 150 rpm. 20 μ l solution was taken in each 1-h interval and continued up to 12 h. ICP-MS was used to measure the concentration of the solution and calculated by putting the values in the following equation-

$$q_e = \frac{(C_o - C_t) \times V}{m} \quad (3)$$

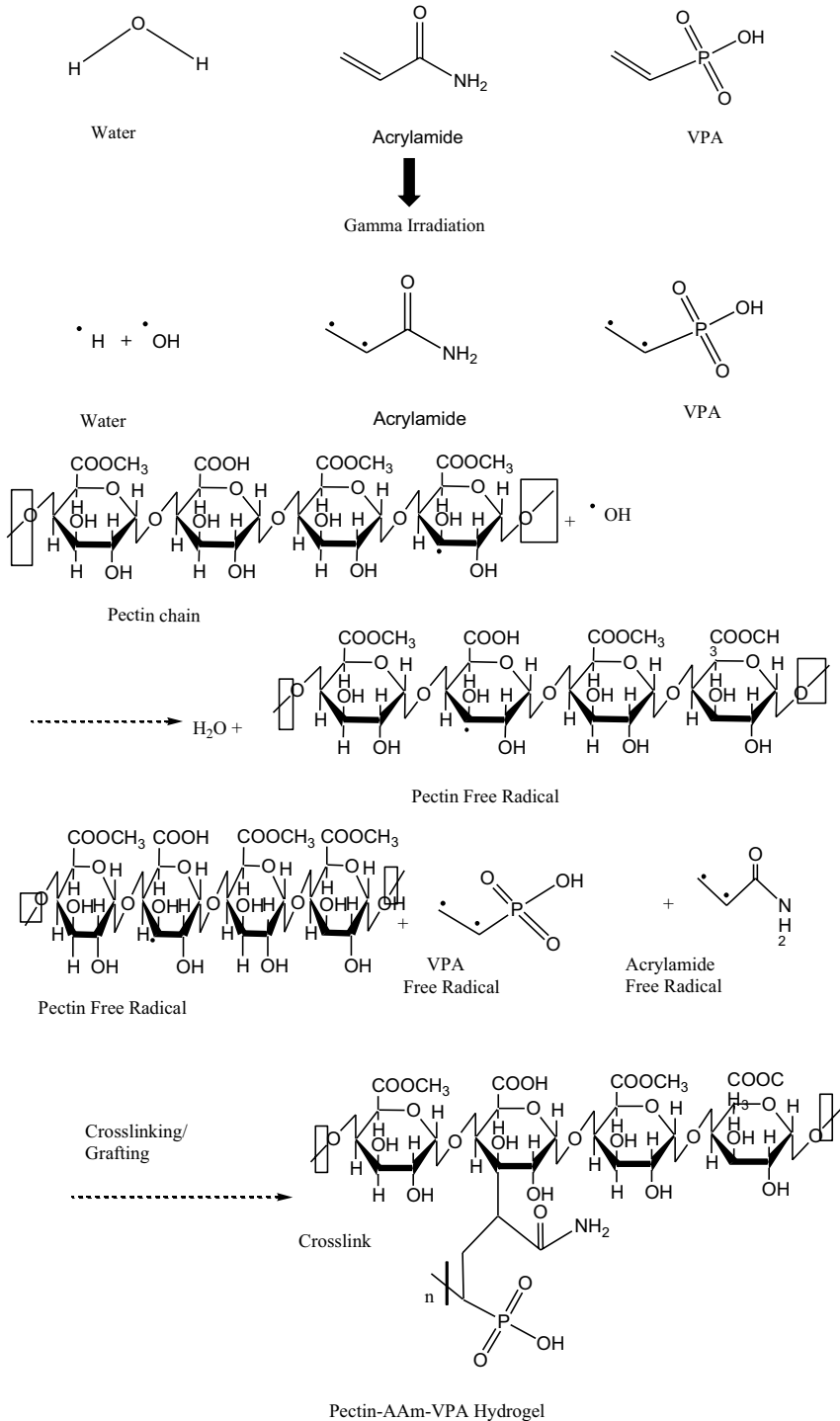
where, C_t concentration of the solution at time t , V is the volume (L) of the solution and, m is the weight of the adsorbent (hydrogel).

For the desorption experiment, metal adsorbed dried hydrogels were immersed in 5% HNO_3 for 12 h and the concentration of the solution was measured accordingly.

Results and discussion

Formation of hydrogel

Gamma radiation belongs to high energy (> 5 keV, < 0.25 Å wavelength, > 12 EHz) electromagnetic radiation that can affect the properties of materials by producing free radicals leading to the formation of copolymer [12]. One of the mostly used



Scheme 1 Probable reaction of Pectin-AAm-VPA hydrogel formation

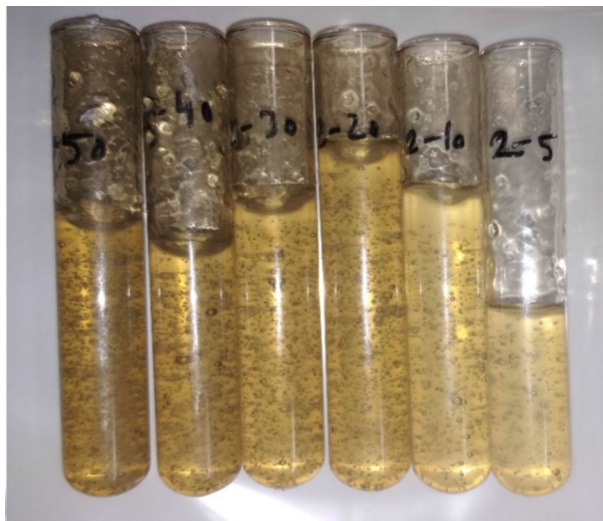


Fig. 1 Pectin–AAm–VPA hydrogels after synthesis

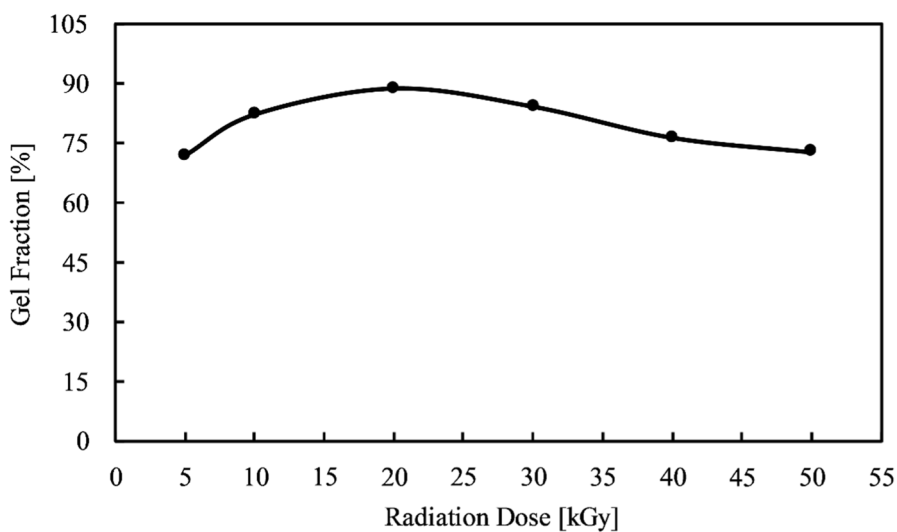
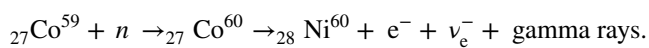


Fig. 2 Effect of radiation dose the gel fraction

sources of gamma ray is Co-60 which is not naturally abundant but can be produced by bombarding a Co-59 with a slow neutron.



Upon exposure to gamma radiation, water molecules break into hydrogen (H $\cdot$) and hydroxyl (OH $\cdot$) free radicals. Hydroxyl free radicals interact with the polymeric backbone of pectin and subtract hydrogen free radicals resulting in the formation of water and pectin free radicals [27].

The molecules containing double bonds interact with radiation in an aqueous medium to produce graft/cross-linked copolymer through the free radical mechanism where no cross-linking agent and reaction initiator is needed [28, 29]. The vinylic monomers Acrylamide and Vinyl phosphonic acid interact with gamma radiation to produce their own free radicals. In the propagation step of polymerization, smaller molecules undergo cross-linking with the pectin backbone to yield Pectin–AAm–VPA polymeric hydrogels. The reaction Scheme 1 shows the probable mechanism of free radical polymerization and hydrogel preparation.

Gel fraction

The most engrossing merits of radiation polymerization are the production of pure gel and better gel yielding. Figure 2 shows the effect of radiation dose on gel yielding of Pectin–AAm–VPA gel where radiation dose started from 2 kGy and ended at 50 kGy. At a very low dose no gel was formed but above 2 kGy gel started to form. At a lower dose, the monomers/polymer cannot be activated enough to produce a sufficient number of free radicals. Gel percentage increases with increasing radiation dose until a maximum at 20 kGy and then starts decreasing up to 50 kGy. The greatest number of raw materials were activated and underwent grafting/cross-linking at 20 kGy and consequently yielded the highest gel product. At higher doses, monomer (AAm, VPA) and natural polymer (Pectin) underwent degradation which decreased the free radical production rate [25, 30]. Vinylphosphonic acid is a small monomer having a phosphonic acid group ($-\text{PO}_3\text{H}$) which interacts with gamma radiation and may undergo degradation resulting in the lower gel percentage compared to other

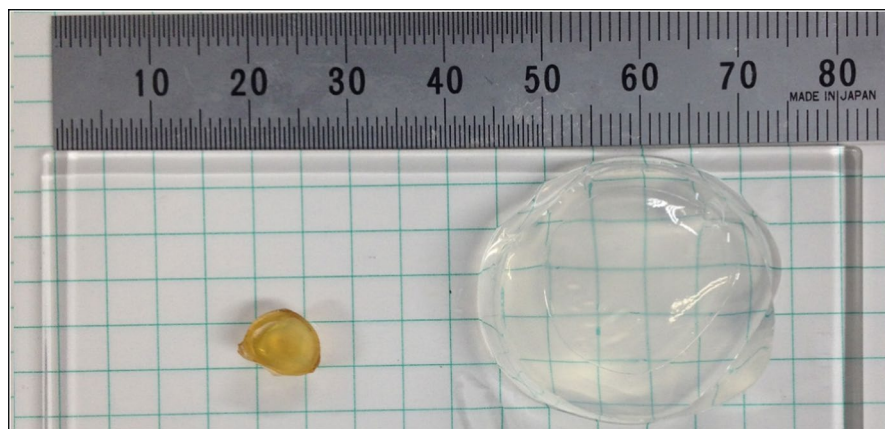


Fig. 3 Pectin–AAm–VPA Hydrogel before and after swelling

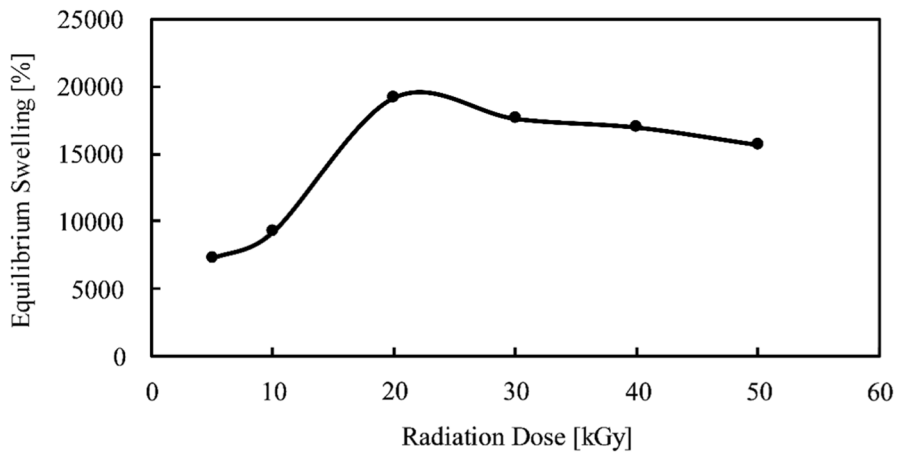


Fig. 4 Effect of radiation dose on equilibrium swelling

radiation-induced hydrogels [31]. However, the optimum gel fraction was found to be 88% for the 20 kGy radiation dose.

Equilibrium swelling

The equilibrium swelling of Pectin–AAm–VPA hydrogels was investigated in an aqueous solution of pH=3. The pre-dried hydrogels were allowed to swell in solution till equilibrium swelling was attained (Fig. 3). The effect of radiation dose on the equilibrium swelling was studied to optimize the radiation dose needed to prepare gels. Figure 4 indicates the increasing trend of swelling from lower dose to upper dose of 20 kGy and then decreasing up to 50 kGy. Hydrogels prepared with lower radiation dose show lower swelling because of less gel content and less availability of functional groups responsible for swelling. At 20 kGy, the largest number of monomers were grafted/cross-linked on the polymeric chain of pectin [32].

Characterization by FTIR spectroscopy

Through the identification of the functional groups by using the Fourier Transform Infrared Spectrophotometer, the grafting/cross-linking of monomers (AAm and VPA) on the pectin backbone was confirmed. Figure 5 represents the FTIR spectra of pristine pectin and Pectin–AAm–VPA gel. In the spectrum of pectin, the peaks at 3292, 2932, 1737, 1512, 1115, and 1010 cm^{-1} are corresponding to –O–H stretching, –C–H stretching, C=O stretching of –COOH, C=O stretching of ester, O–C–C stretching, and C–O stretching vibration, respectively. In the spectrum of Pectin–AAm–VPA gel, the distinguishable peaks are at 3183 cm^{-1} for N–H stretching overlapped with O–H of –COOH, 1651 cm^{-1} for P–O–H bending, 1450–1401 cm^{-1} range of peak for C–H bending, 1100 cm^{-1} for P=O stretching of Phosphonic acid group, 966–915 cm^{-1} range for P=O stretching of –PO₃H, respectively. C=O

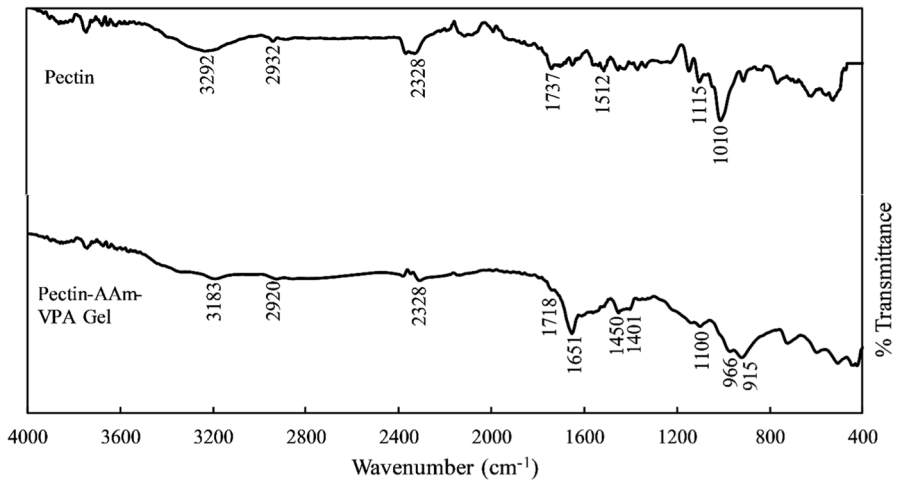


Fig. 5 FTIR spectra of Pectin powder and Pectin–AAm–VPA gel

stretching at 1718 cm^{-1} after grafting of monomer. A weak peak at 2328 cm^{-1} in both spectrums is for atmospheric carbon dioxide (CO_2). The presence of N–H stretching peak indicates the presence of acrylamide as linker between pectin and VPA monomer. So, the FTIR report gives strong proof for the successful preparation of Pectin–AAm–VPA gel.

Differential scanning calorimetry (DSC)

Thermal properties of Pectin–AAm–VPA gel prepared by applying 20 kGy radiation dose and pectin were studied by using differential scanning calorimetry (DSC). Figure 6 represents the thermogram of pectin and the VPA gel where the glass transition (T_g) and melting (T_m) temperature of pristine pectin powder (Fig. 6a) are at 84 and 151 °C [33]. The initial inclination of the DSC curve (Fig. 6b) indicates the glass transition (T_g) at 102 °C temperature, then the melting temperature (T_m) at 187 °C which are higher than pectin powder. Therefore, the hydrogel is thermally stable enough to be used in various fields.

Adsorption and desorption of multielement

The Pectin–AAm–VPA gels were applied in metal adsorption from a multielement solution and investigated whether the gel adsorbents are selective toward a specific metal ion or a group of metal ions. Figure 7 exhibits the selective metal ion adsorption and desorption. Figure 7a depicts the adsorption capacity of gels where among

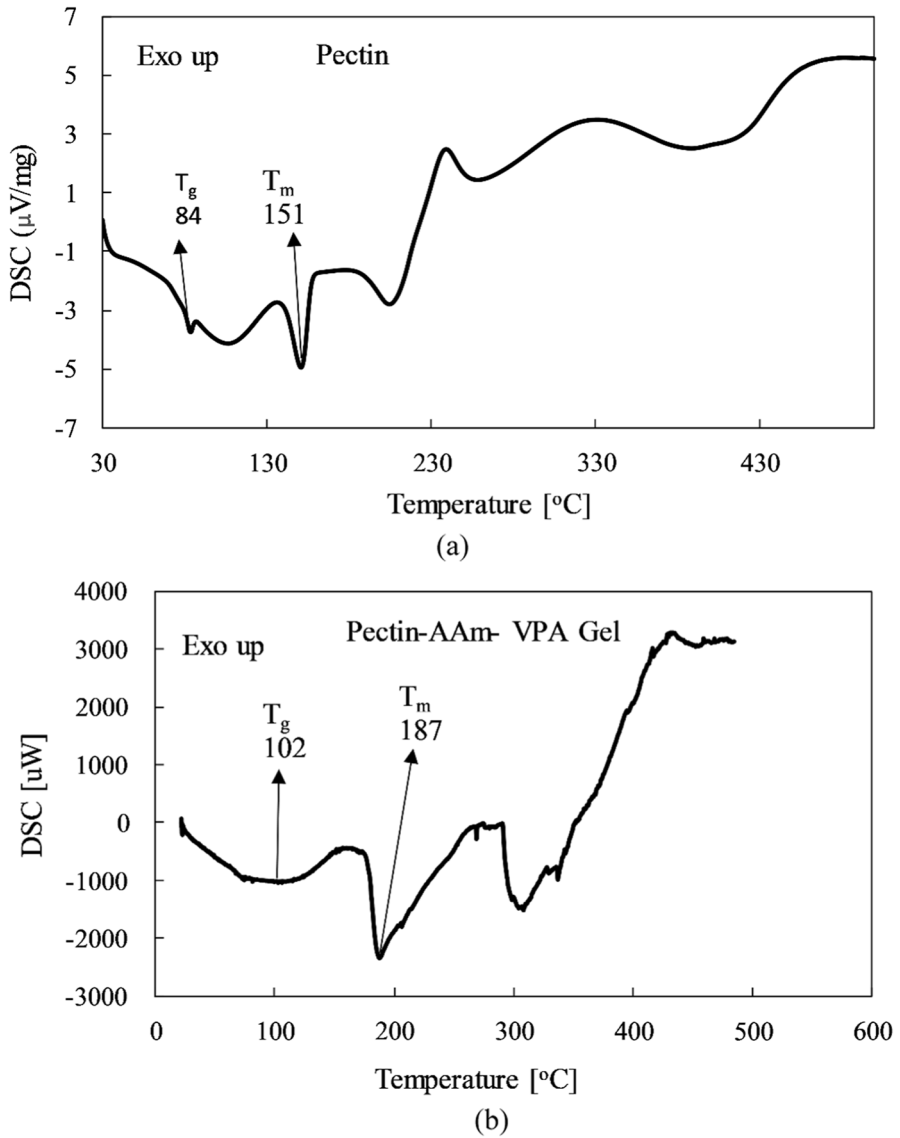
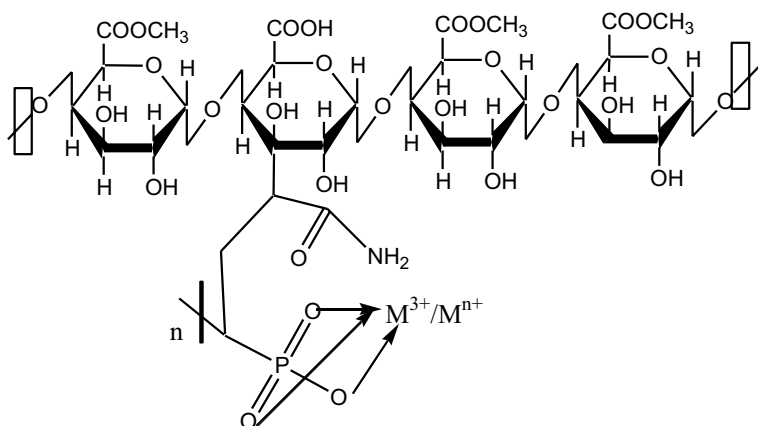


Fig. 6 DSC thermogram of **a** Pectin and **b** Pectin-AAm-VPA gel

the 27 metal ions, the highest selectivity was toward Aluminum (Al), Iron-II (Fe), Gallium (Ga), Molybdenum (Mo), Indium (In) and Bismuth (Bi). Along with the above metals very little adsorption of Vanadium (V) and Beryllium (Be) may take place. The phosphonic acid part of the hydrogel is the ionic part which can show



Scheme 2 Probable mechanism of metal adsorption by Pectin–AAm–VPA hydrogel

electrostatic attraction with metal ions through hydrogen (H^+) ion substitution. The competition of electrostatic attraction between phosphonate ion and metal ion may be the predominant matter of selective adsorption (Scheme 2). The cause of selectivity may also be attributed to the size and charges of the metal ions which may facilitate interaction with the phosphonic acid group easily. Figure 7b indicates the desorption of metal ions from the void space and surface of the hydrogels to 5% nitric acid. It is clear from the bar diagram that the metal ions can be desorbed successfully and the gels reused. The hydrogels prepared by 20 kGy radiation dose, show the maximum adsorption and desorption capacity (Fig. 7c). Hence, the optimization of radiation dose for Pectin–AAm–VPA hydrogel synthesis is also supported well. Ondrej et al. extracted Ga^{3+} from the solution of two metals- Al^{3+} and Ga^{3+} on graphite oxide [34]. Wentao Li et al. reported the removal of trace amount of Al^{3+} selectively from the binary mixture of Nd^{3+} , Ca^{2+} using grafted silica gel [35]. Cui-hua et al. used sulfonated cellulose to remove Fe^{3+} , Pb^{2+} and Cu^{2+} from wastewater [36]. In the previous research we studied the selective adsorption of Silver (Ag^+) ion from the multielement solution [25]. There are very few research reports on the selective adsorption of metal adsorption from the solution of 27 elements.

Table 3 Elements in SEM-EDS analysis of Pectin–AAm–VPA hydrogel before and after metal adsorption

Material	Presence of elements
Hydrogel before metal adsorption	Phosphorus (P), Oxygen (O), Nitrogen (N), and Carbon (C)
Hydrogel after metal adsorption	Phosphorus (P), Oxygen (O), Nitrogen (N), and Carbon (C), Aluminium (Al), Iron (Fe), Gallium (Ga), Indium (In) and, Molybdenum (Mo)

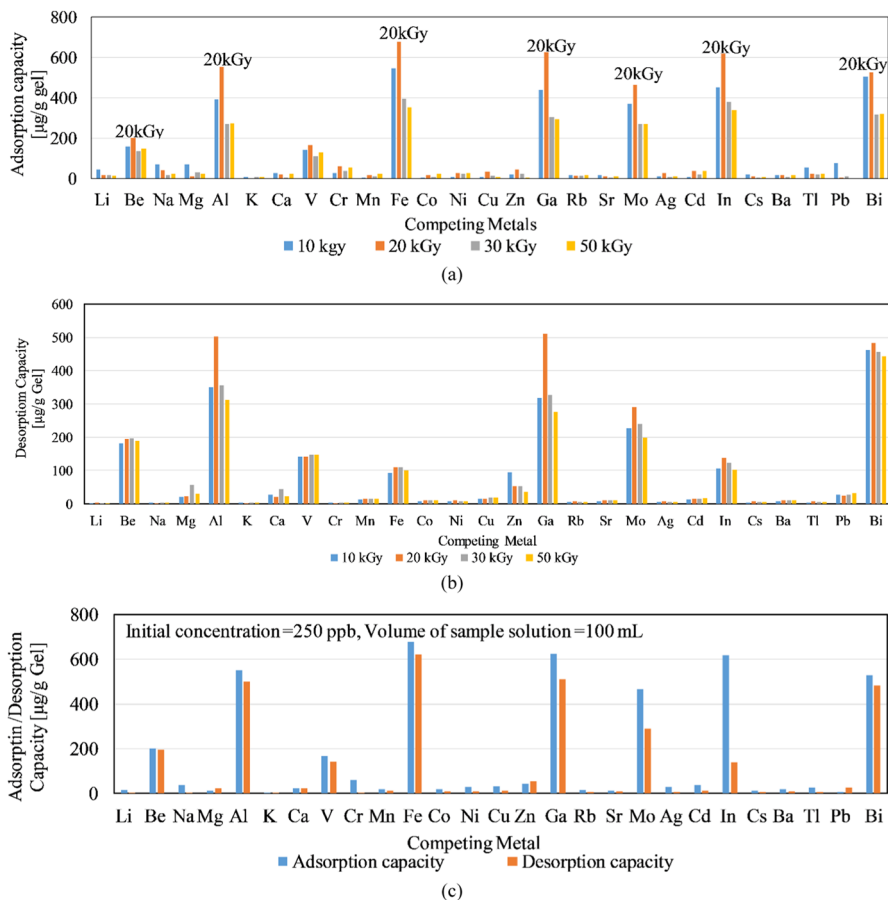
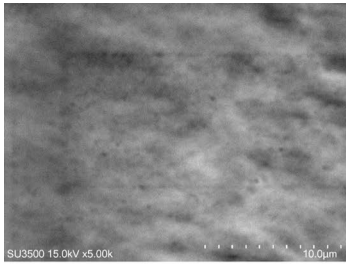


Fig. 7 Multielement adsorption/desorption by Pectin-AAm-VPA hydrogels at pH=3 **a** metal adsorption on hydrogels prepared by all radiation doses **b** desorption from the hydrogels and **c** adsorption-desorption by hydrogel prepared by 20 kGy dose

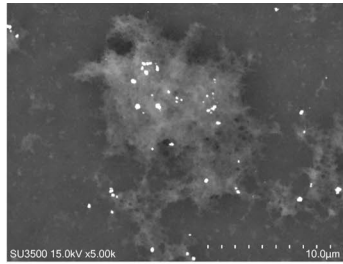
SEM-EDS analysis of hydrogel before and after multielement adsorption

The surface morphology of Pectin-AAm-VPA hydrogels before and after metal ion adsorption was studied using scanning electron microscopy (SEM) equipped with energy-dispersive X-ray spectroscopy (EDS). Figure 8 reflects the SEM-EDS images of gel before and after metal adsorption. SEM image reflects a smooth and plain surface of only gel along with EDS analysis results highlighting the presence of Phosphorus (P), Oxygen (O), Nitrogen (N), and carbon (C) as constituent's

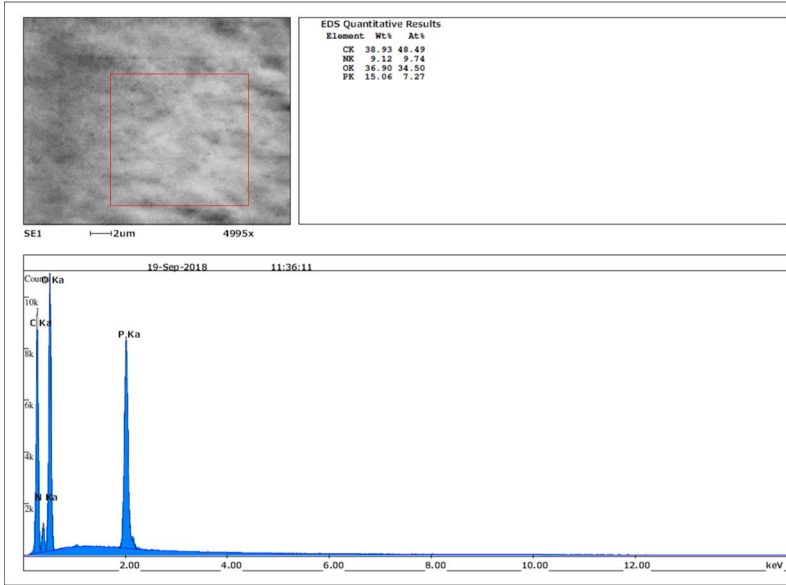
Fig. 8 SEM-EDS of Pectin-AAm-VPA gel before and after metal adsorption **a** hydrogel surface before metal adsorption **b** hydrogel surface after metal adsorption **c** SEM-EDS of hydrogel before metal adsorption and **d** SEM-EDS after metal adsorption at pH=3



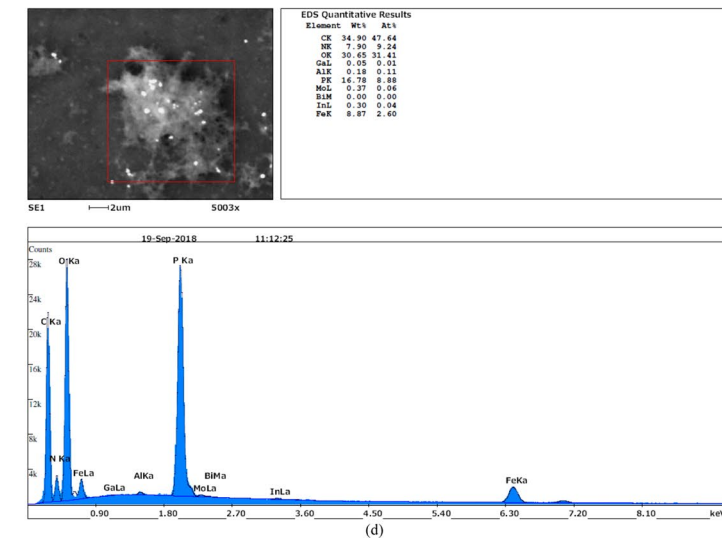
(a)



(b)



(c)



(d)

elements. The presence of Nitrogen (N) and Phosphorus (P) in the EDS supports the amide ($-\text{NH}_2$) and phosphonic ($-\text{PO}_3\text{H}$) acid groups in the hydrogel. After multi-element adsorption SEM image reflects the spotted surface instead of smooth pristine gel. The quantitative results of EDS give clear peak for Al, Fe, Ga, In and, Mo which confirms the selective adsorption of those metals (Table 3). The absence of Vanadium and Beryllium can be attributed to the little absorption in the void space of gel or due to experimental error.

Conclusion

Pectin–AAM–VPA hydrogels were synthesized successfully by applying gamma radiation and investigated the selective adsorption of metal ion/ions. On the basis of gel content 88% and equilibrium swelling $\sim 20,000\%$ per gram of gel at $\text{pH}=3$, the radiation dose for Pectin–AAM–VPA (5% Pectin + 10% AAM + 15% VPA) hydrogel synthesis was optimized to be 20 kGy. FTIR spectrum confirmed the expected functional groups in the gel as well as grafting/cross-linking between monomers (AAM, VPA) and pectin. DSC analysis revealed that the hydrogel is thermally stable enough to be used in metal adsorption. The most interesting part of this research is that, hydrogels are highly selective to a few metals (Al, Fe, Ga, In, Mo, and Bi) among 27 metals of the multielement solution. The selective adsorption was confirmed by SEM–EDS analysis of the hydrogel surface before and after metal ion adsorption. Desorption of the metal ions from hydrogel to 5% nitric acid also shows efficiency of more than 90%. Therefore, all results suggest that the Pectin–AAM–VPA hydrogels can be useful in selective metal adsorption and the authors intend to do further study on adsorption isotherm and kinetics in detail.

Author contributions MMB contributed to conceptualization, investigation, methodology, validation, data curation, funding acquisition, and writing—original draft. MJ contributed to writing—review and editing. J-HJ contributed to review, editing and Advisor.

Dataset BHUYAN, MD (2022), “Pectin-Acrylamide-VinylPhosphonic acid hydrogel”, Mendeley Data, V1, <https://doi.org/10.17632/9t93wv5t9f.1>.

Declarations

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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