Flame-Retardant and Morphological Analysis of Nitrogen Heterocycle-Modified Poly(vinyl alcohol) and Their Application for Adsorption of Heavy Metal Ions

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ABSTRACT: The functional modification of poly (vinyl alcohol) (PVA) was conducted through phosphorus containing nitrogen heterocycles. This has been believed to have extensive thermal stability and heavy metal ion adsorption in the area of polymers. The heterocyclic modified polymers were characterized by Infra red (FTIR), Nuclear magnetic resonance spectroscopy, and elemental analysis. Thermogravimetric analysis studies displayed that phosphorus-containing five membered and fused heterocyclic based PVA were less thermally stable than six membered compounds. Differential scanning calorimetric studies reported that the glass transition and melting point temperature of the heterocyclic modified PVA was higher than the pure PVA. X-ray diffraction studies were done to analyze the structure of the modified polymer. Atomic force microscopy surface scans showed that the modified polymeric surface was found to have rough in micrometer scale. Modified PVA showed improved thermal stability, flame retardance, organosolubility, and surface roughness. The adsorption capacities of the modified PVA were determined for several heavy metal ions with the variation of pH. The adsorption capacity was found as 289 mg Pd^{2+}/g of imidazole modified PVA and exhibited higher than other modified PVA. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 129: 2046–2056, 2013

INTRODUCTION

Poly(vinyl alcohol) (PVA) is a nontoxic, water-soluble, biocompatible, and biodegradable polymer, which is widely employed in various applications such as fibers for cloth industries, films, membranes, materials for drug delivery system, and cancer cell-killing embolic materials.[1] PVA fibers, gels, and films are potentially high-performance materials because they have high tensile strength and modulus, excellent impact strength, high abrasion resistance, excellent alkali resistance, and oxygen barrier property.[2]

Functional modification of PVA or introduction of reactive functional groups into the polymer chain has been believed to have basic significance while expanding its application. Many researchers have reported about the modification of polymer for the purpose of introducing carboxylic, sulfonate, and amino groups[3,4] for specific applications. Synthesis of PVA that contains phosphorus and heteroaromatics in the polymer chain attracted the attention of many researchers due to their peculiar characteristics viz., nonflammability, thermal stability, high melting points, heavy metal ion extraction properties.[5,6] Among the nitrogen heterocycles, six-membered heterocyclic compounds are used in various applications such as herbicides, insecticides, pharmaceuticals, and adhesives whereas five-membered heterocyclic compounds are used in electrical and pharmaceuticals applications.[7]

Incorporation of P=O unit into PVA showed improved flame retardancy, thermal oxidative stability and good adhesion.[8] Phosphorylated PVA has attracted considerable interest because of its nonflammability, metal complexes, anionic polyelectrolyte hydrogels, and cation exchange resins. Phosphorus-containing polymers meet the requirements of low toxicity and low smoke during combustion for environmental and health considerations. Phosphorus-containing polymers are able to increase the char while burning, which decreases the amount of flammable zone and reduce the heat transfer from the flame to the material.[9–11] Therefore, in this article, the PVA was chemically modified with phosphorus-based nitrogen heterocycles and well characterized using Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR) spectroscopy. In addition we have studied the flame retardant, solubility, morphology, and heavy metal adsorption activities.

EXPERIMENTAL PART

Materials

PVA (MW = 14,000) with a degree of hydrolysis of 98–99% and phosphorus oxychloride was supplied by SD Fine Chemicals, India. Piperidine, piperazine, indole, imidazole, and 1,2,4-triazole were purchased from Sigma-Aldrich, Mumbai, India. Triethylamine was obtained from Qualigens Fine Chemicals, Mumbai, India. Organic solvents like toluene, chloroform, acetone, methanol, DMF, and DMSO have been received as analytical grade from SD Fine Chemicals, India. All solvents were distilled before use. The stock solutions of metal ions (1000 mg L^{-1}) were prepared by dissolving appropriate amounts of chemicals in 10 mL of concentrated HCl and HNO$_3$ that makes the volume to 1 L. These solutions were standardized and working solutions of the metal ions were made by their suitable dilution with double distilled water. The chemicals used for the solution were cadmium (II) iodide, chromium (II) chloride hexahydrate, copper (II) sulfate pentahydrate, nickel (II) sulfate hexahydrate, zinc (II) sulfate heptahydrate, lead (II) nitrate, ferric chloride, and mercuric chloride.

Characterization Methods

Infrared spectra were measured as KBr pellets with a midrange of 500–4000 cm^{-1} using the Thermo Nicolet 330 FTIR spectrometer. Elemental analysis was carried out on EI III, Carlo Erba 1108 elemental analyzer with the detection limit from 0.1 to 1 μg. The exact molecular weight of the intermediates was measured from JEOL GCMATE II GC-MS spectrometer with a high resolution data system. X-ray diffraction (XRD) analysis was performed for the unmodified and modified PVA with D8 advance BRUKER X-ray diffractometer with Cu-target (λ = 1.5418 Å) and Ni filter.

Thermal Analysis. Thermogravimetric analysis (TGA) has been carried out using a Netzsch STA 409 simultaneous thermal analyzer. The samples were heated from 35 to 900°C at a heating rate of 10°C/min under a nitrogen atmosphere.

Flame retardance can also be evaluated from the char residue on pyrolysis. Van Krevelen has established a linear relationship between limiting oxygen index (LOI) and char residue for halogen free polymers.[12] The LOI was calculated by using Van Krevelen's equation[12]

$$LOI = 17.5 + 0.4(\sigma)$$

where σ is the percentage of char yield.

The crystalline melting point and glass transition temperature of the polymers have been determined by Netzsch DSC 204 differential scanning calorimeter (DSC).

AFM Analysis. Polymer of 0.5 μM concentration were dissolved in DMSO and used for atomic force microscopy (AFM) study. This has been deposited on silicon glass substrates and allowed to dry at 50°C for 30 min in vacuum oven. AFM has been recorded under ambient conditions using VEECO CP2 instrument. The height images have been obtained from tapping mode AFM. Silicon cantilever tips at a resonance frequency of ∼ 300 kHz and spring constant of about 40 nm^{-1} were used.

The amplitude properties are mainly described by six parameters, such as roughness average (Sa), root mean square roughness (RMS) (Sq), peak-peak height (Sy), maximum peak valley depth (Sv), mean value (Sm), and maximum peak height (Sp). These parameters describes about the information of statistics average properties, the shape of the height distribution histogram and extreme properties. These parameters were determined by a built-in-image processing toolbox in the AFM software.

Swelling Studies. Modified and unmodified PVA samples were immersed in distilled water for 24 h at room temperature until the sample reached the equilibrium state of swelling. The samples were taken out from the water, dried with filter paper, and the mass was determined. The percentage of swelling (water absorptivity) was calculated.

$$\text{Percentage of swelling} = \frac{(W_2 - W_1)}{W_1} \times 100$$

where W_1 is the original weight of the sample and W_2 is the weight of the swollen sample.

Metal Adsorption Procedure

Adsorption Capacity Test. Twenty five milliliter of metal ions with different initial concentration which was adjusted to the desired pH with hydrochloric acid (or nitric acid) or sodium hydroxide aqueous solution (0.1 mol L^{-1}) was added to dry 5 mg modified PVA samples. After stirred for 8 h at room temperature, the mixture was filtered. The metal ions concentration in the filtrate and initial concentration were determined by atomic absorption spectrophotometer (AAS). The adsorption capacities were calculated as follows:

$$q = \frac{(C_0 - C)_V}{m}$$

where q is an adsorption capacities of polymer (mg of metal ion/g of adsorbent), v is the volume of metal ion solution, C_0 is the concentration of metal ion before adsorption (mg L^{-1}), C is concentration of metal ion after adsorption (mg L^{-1}), and m is the weight of modified PVA samples (g).

Effect of pH. Twenty five milliliter of aqueous solution of metal ions with different initial pH value was added to 5 mg modified PVA samples. Dilute hydrochloric acid and sodium hydroxide solutions were used to adjust the initial pH value from 2 to 7. After stirred for 8 h at room temperature, the mixture was filtered. The metal ions concentration in the filtrate and initial concentration were determined.

Preparation of *N*-heterocyclic Phosphonyl Dichloride Moieties

In a three-necked 250 mL reaction flask fitted with a condenser, thermometer, and a pressure equalizing dropping funnel are assembled. One millimolar (0.068 g) of imidazole and 2 mmol (0.153 g) of phosphorus oxychloride were dissolved separately in 20 mL of tetrahydrofuran (THF) each and added slowly one over the other using additional funnel with constant stirring for 15 min at 0–5°C in the presence of catalytic amount of

Scheme 1. Synthetic routes of heterocyclic modified PVA.

triethylamine. The reaction was continued for 24 h at room temperature. The reaction mixture was washed three times with water. The organic layer was separated out and distilled off the solvent to get residue. The residue was purified by column chromatography through silica gel and chloroform. The final product has been isolated and dried in vacuum at 50°C. The same procedure was adopted for 1,2,4-triazole, piperidine,

piperazine, and indole to get various *N*-heterocyclic phosphonyl dichlorides, respectively. These are displayed in Scheme 1.

1H-imidazole-1-phosphonyl dichloride (2a). Light brown precipitate (0.14 g, 67%). FTIR (KBr, cm^{-1}): 2969 (aromatic CH stretching), 1222 (P=O), 1060 (P—N), 479 (P—Cl). ^{1}H NMR (CDCl$_3$, ppm): 7.3 (d,2H), 7.7 (s,1H). ^{13}C NMR (CDCl$_3$, ppm):

138.6, 127.7, 122.32. (imidazole carbons) HRMS calculated for $C_3H_3Cl_2N_2OP$ m/z = 183.9460, found 183.1880.

1H-1,2,4-triazole-1-phosphonyl dichloride (2b). Colorless liquid (0.12 g, 58 %). FTIR (KBr, cm^{-1}): 2927 (aromatic CH stretching), 1259 (P=O), 1016 (P—N), 488 (P—Cl). ^{1}H NMR (CDCl$_3$, ppm): 7.7 (s,1H), 7.8 (s,1H). ^{13}C NMR (CDCl$_3$, ppm): 150.12, 151.32 (triazole carbons). HRMS calculated for $C_2H_2Cl_2N_3OP$ m/z = 184.9313, found 185.1202.

Piperidine-1-phosphonyl dichloride (2c). Light brown precipitate (0.12 g, 63%). FTIR (KBr, cm^{-1}): 2840 (aliphatic C—H stretching), 1240 (P=O), 1022 (P—N), 452 (P—Cl). ^{1}H NMR (CDCl$_3$, ppm): 1.8 (t,3H), 2.8 (s,1H). ^{13}C NMR (CDCl$_3$, ppm): 25.12, 23.46, 23.54, 48.2, 49.4 (piperidine carbons). HRMS calculated for $C_5H_{10}Cl_2NOP$ m/z = 200.9880, found 199.8587.

Piperazine-1, 4-diphosphonyl dichloride (2d). Light brown precipitate (0.17 g, 62%). (4 mmol of phosphorus oxychloride was taken because it reacts with both the acidic protons). FTIR (KBr, cm^{-1}): 2838 (aliphatic C—H stretching), 1233 (P=O), 1047 (P—N), 486 (P—Cl). ^{1}H NMR (CDCl$_3$, ppm): 2.7 (t, 2H), 2.9 (t, 1H). ^{13}C NMR (CDCl$_3$, ppm): 43.21, 43.13, 43.79, 44.12 (piperazine carbons). HRMS calculated for $C_4H_8Cl_4N_2O_2P_2$ m/z = 319.2718, found 319.0.

1H-indole-1-phosphonyl dichloride (2e). Dark brown precipitate (0.12 g, 69%). FTIR (KBr, cm^{-1}): 2920 (aromatic C—H stretching), 1269 (P=O), 1067 (P—N), 466 (P—Cl). ^{1}H NMR (CDCl$_3$, ppm): 7.3 (t, 2H),7.7 (s, 1H),7.2 (d, 1H), 6.8 (d, 1H), 6.5 (d, 1H). ^{13}C NMR (CDCl$_3$, ppm): 137.61, 128.12, 127.7, 122.32, 119.19, 111.01, 102, 103 (indole carbons). HRMS calculated for $C_8H_6Cl_2NOP$ m/z = 234.9130, found 234.

Functional Modification of PVA Using *N*-heterocyclic Phosphonyl Dichloride Moieties

The synthetic procedure for the modification of PVA was followed from our previous literature report.[13] In a 250 mL three necked round bottom flask, 6 mmol of PVA and triethylamine was dissolved in 50 mL of DMF under inert atmosphere. Then, 1 mmol of *N*-heterocyclic phosphonyl dichloride (**2a-2e**) in 50 mL DMF was added dropwise to the reaction flask and maintained the temperature at 90°C for 12 h with constant stirring. The white triethylamine hydrochloride was removed from the reaction mixture by filtration. The solvent was removed under reduced pressure and the generated product was washed with toluene or methanol (depends on acid chloride used). The final modified PVA was dried at 60°C using vacuum oven.

Poly(divinyl 1H-imidazol-1-yl-1-phosphonate) (3a). Light brown waxy polymer (Yield: 85 %). FTIR (KBr, cm^{-1}): 3436 (OH), 3064 (Aromatic CH), 1446 (P—Ph), 1237 (P=O), 1013 (P—N), 1117 (P—O—C). ^{1}H NMR (DMSO-d$_6$, ppm): 8.3–8.9 (imidazole protons), 4.2, (—OH), 2.3–2.7 (CH$_2$), 4.0 (CH—).^{13}C NMR (DMSO-d$_6$, ppm): 124–128 (imidazole carbons), 52.14–53.80 (O—CH—), 44.32–44.70 (CH$_2$), ^{31}P NMR (DMSO-d$_6$, ppm): 1.725. Elemental Analysis (%): C, 40.57; H, 13.16; N, 3.82.

Poly(divinyl 1H-1, 2, 4-triazol-1-yl-1-phosphonate) (3b). White waxy polymer (Yield: 75%). FTIR (KBr, cm^{-1}), 3401 (OH), 3125

(Aromatic CH), 1454 (P—Ph), 1223 (P=O), 1048 (P—N).1150 (P—O—C). ^{1}H NMR (DMSO-d$_6$, ppm): 7.1 (triazole protons), 3.2–3.4, (—CH—), 1.2–1.3 (CH$_2$), 1.32–1.33 (OH—). ^{13}C NMR (DMSO-d$_6$, ppm): 159 (triazole carbons), 63.50–65.96 (O—CH—), 45.79–55.43 (CH$_2$), ^{31}P NMR (DMSO-d$_6$, ppm): 2.860. Elemental Analysis (%): C, 56.59; H, 12.26; N, 4.03.

Poly (divinyl piperidin-1-yl-1-phosphonate) (3c). Light brown waxy polymer (Yield: 80%). FTIR (KBr, cm^{-1}): 3422 (OH), 2873 (Aliphatic CH), 1456 (P—Ph), 1210 (P=O), 1073 (P—N).1161 (P—O—C). ^{1}H NMR (DMSO-d$_6$, ppm): 1.9 (piperidine protons), 3.9–4.0, (—CH—), 1.3 (CH$_2$), 3.6 (OH—). ^{13}C NMR (DMSO-d$_6$, ppm): 20.84 (piperidine carbons), 63.27–65.49 (O—CH—), 40.27–40.60 (CH$_2$), ^{31}P NMR (DMSO-d$_6$, ppm): 2.318. Elemental Analysis (%): C, 48.13; H, 13.18; N, 2.76.

Poly (tetravinyl piperazin-1, 4-diyl-1, 4-bis (phosphonate)) (3d). Dark brown waxy polymer (Yield: 78%). FTIR (KBr, cm^{-1}): 3406 (OH), 2845 (aliphatic CH), 1467 (P—Ph), 1236 (P=O), 1063 (P—N).1152 (P—O—C). ^{1}H NMR (DMSO-d$_6$, ppm): 1.89 (Piperazine protons), 3.1–3.4, (—CH—), 1.6 (CH$_2$), 2.1 (OH—).^{13}C NMR (DMSO-d$_6$, ppm): 30.25 (piperazine carbons), 61.92–67.62 (O—CH—), 47.24–51.18 (CH$_2$). ^{31}P NMR (DMSO-d$_6$, ppm): 2.308, −2.318. Elemental Analysis (%): C, 35.14; H, 12.63; N, 3.82.

Poly (divinyl 1H-indol-1-yl-1-phosphonate) (3e). Dark brown waxy polymer (Yield: 82%). FTIR (KBr, cm^{-1}): 3437 (OH), 3145, (Aromatic C—H), 1411 (P—Ph), 1383 (P=O),1047 (P—N).1191 (P—O—C). ^{1}H NMR (DMSO-d$_6$, ppm): 6.92–7.9(Indole protons), 3.47–3.89 (—CH—), 1.09–1.48 (CH$_2$), 4.26 (OH—).^{13}C NMR (DMSO-d$_6$, ppm): 116–130 (Indole carbons), 64.35–66.59 (O—CH—), 45.14–46.24 (CH$_2$). ^{31}P NMR (DMSO-d$_6$, ppm): 1.826. Elemental Analysis (%): C, 59.36; H, 12.32; N, 2.62.

RESULTS AND DISCUSSION

A nonreactive flame retardant consisted of phosphorus and nitrogen, which gives a "synergistic flame retardation effect" to the polymeric material.[14] The presence of phosphorus and nitrogen compositions in the polymer promoted the char formation at high temperature. However, this polymer main chain consisted of N—P—O bonds, which exhibited a lower degradation temperature.[15] Therefore, three different heterocyclic compounds were selected for the synthesis, such as five membered heterocyclic compound viz., imidazole (**1a**), triazole (**1b**), six membered heterocyclic compound viz., piperidine (**1c**), piperazine (**1d**), and fused heterocyclic compound of indole (**1e**), respectively. These *N*-heterocyclic compounds have free acidic protons reacted with phosphorus oxy chloride at 0°C to get reactive flame retardant *N*-heterocyclic phosphonyl dichloride compounds **2(a-e)**.[16]

N-heterocyclic group of these compounds were reactive towards PVA hydroxyl group. The C—O—P bonds formed to link the polymer chain and lateral P—N bonds formed to crosslink the polymers (Scheme 1). Functional modification of PVA with phosphorus containing *N*-heterocycles **3(a-e)** have been believed to have extensive thermal stability and metal ion adsorption activity. Moreover, theoretical value of high contents of phosphorus (13.2–19.3%) and nitrogen (6.9–22.6%) are present in the
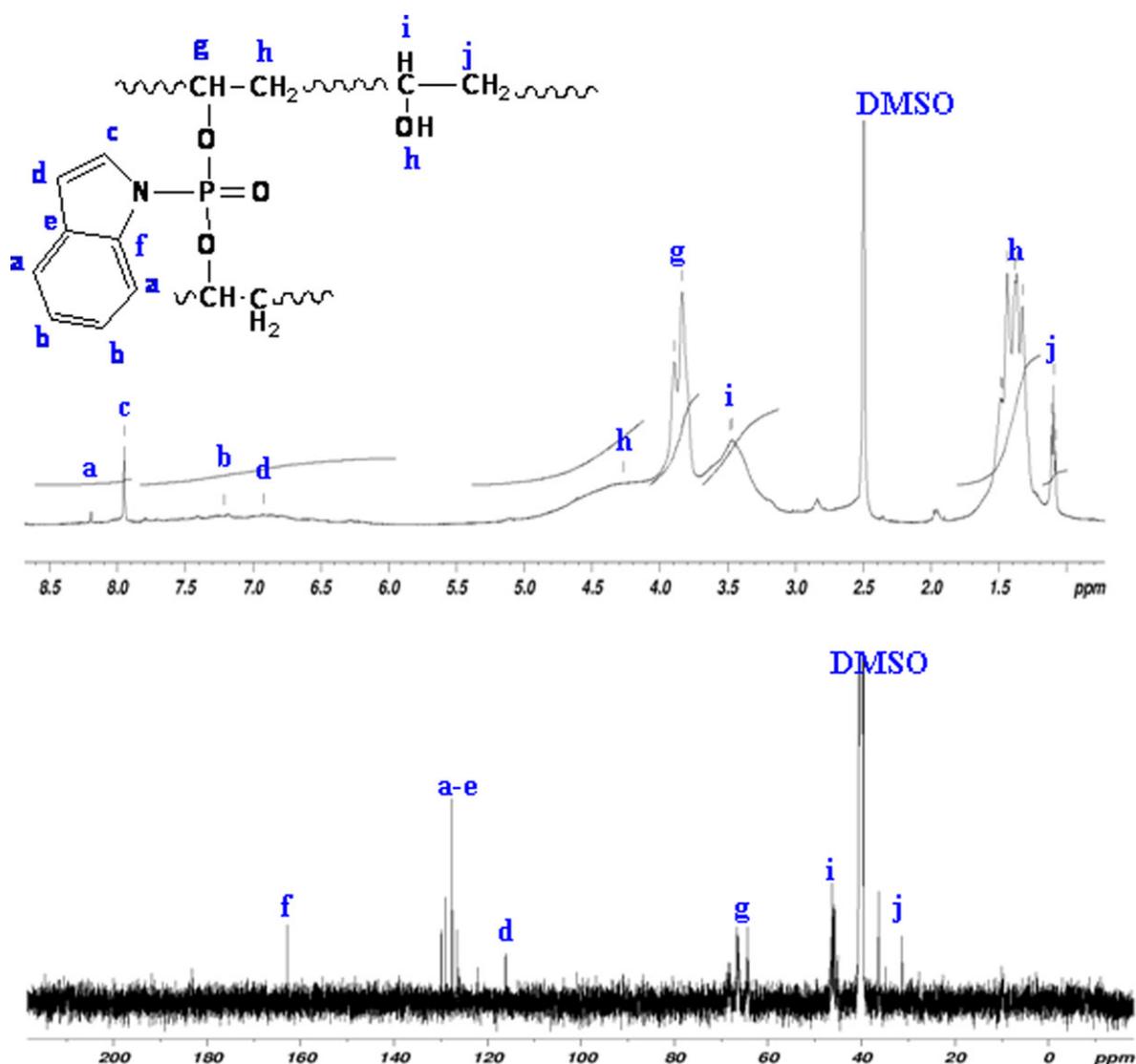
Figure 1. ^{1}H NMR and ^{13}C NMR spectra of indole modified PVA (**3e**). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

heterocyclic compounds **2(a-e)**, which was used to modify the PVA system. The final modified PVA exhibits better flame retardancy than the original PVA. *N*-heterocyclic compounds with phosphorus groups **2(a-e)** are not only serves as flame retardant but also gives good metal ion adsorption activity to the PVA. PVA reacted with *N*-heterocyclic phosphonyl dichloride **2(a-e)** at 90°C in a solution of DMF and it gives a network of phosphorus containing *N*-heterocyclic group (imidazole, triazole, piperidine, piperazine, and indole) functionalized PVA **3(a-e)**. Formation of the modified PVA product strongly confirmed by spectral studies viz., FTIR, NMR, thermal analysis and found the metal ion adsorption activity.

Spectral Studies
FTIR analysis was carried out to study the change in structure of PVA before and after heterocyclic phosphorylation. FTIR spectra of PVA shows a sharp peak of OH bending at 1293 cm^{-1} but the transmittance peak decreased gradually in

phosphorylated PVA **3(a-c)**. Thus, modification of PVA by heterocyclic phosphorylation causes a decrease in percentage transmittance (%T) for OH groups. Large and small OH transmittance peak were found for piperazine (**3d**) and indole (**3e**) modified PVA, respectively. The trend was also supported by elemental analysis through a degree of modification. A new peak appeared at 1117–1191 cm^{-1} and 1210–1283 cm^{-1} for P—O—C stretching and P=O stretching, respectively. The P—N stretching of heterocyclic modified polymers revealed another peak at 1013–1173 cm^{-1}. Moreover, the disappearance of P—Cl stretching and formation of P—O—C and P—N stretching band confirms the formation of the modified PVA **3(a-c)**.

Figure 1 shows the ^{1}H and ^{13}C NMR spectrum of the indole modified PVA (**3d, 3e**) in detail. Because of the incorporation of *N*-heterocyclic compounds the following observation were found from ^{1}H NMR spectrum. The peak appeared at around 6.9–8.9 ppm implies that the modified PVA **3a, 3b, 3e** possesses aromatic heterocyclic protons. The peak at 1.9 ppm expresses that the **3c,**

Table I. Elemental Analysis of Modified Polymers

Polymers	Elemental analysis (%)			Degree of modification
	C	H	N	
3a	40.57	13.16	3.82	57.5
3b	56.59	12.26	4.03	72.8
3c	48.13	13.18	2.76	64.1
3d	35.14	12.63	3.82	51.6
3e	59.36	12.32	2.62	74.3

3e polymers possesses aliphatic heterocyclic protons. From the ^{13}C NMR spectrum, the product **3a** shows signals at 124–128 ppm corresponded to imidazole carbons. The product **3e** shows the peak at 116–130 ppm, which confirms the presence of indole carbons. A singlet peak at 20.8 and 30.2 ppm supports the presence of same environmental piperidine and piperazine carbons in the polymer **3c** and **3d.** The signal at 151 ppm represents the two carbons of triazole (**3b**) present in the same environment. Singlet of 63-65 and 40-45 ppm formed in all heterocyclic modified PVA **3 (a-e)** which corresponds to methylene and methine peaks of PVA, respectively.

The presence of phosphorus atom in modified polymer was confirmed from ^{31}P NMR spectroscopy. Only one phosphorus signal was observed at 1.725, 2.860, 2.318, and 1.826 ppm for the polymers **3a, 3b, 3c, and 3e,** respectively. But, two peaks were noticed at 2.306 and −2.318 ppm for piperazine modified PVA (**3d**). This is because of phosphorus (P=O) situated in two opposite direction in piperazine moiety.

Elemental Analysis

Elemental analysis report of the modified polymers **3(a-e)** were shown in Table I. The degree of modification was calculated from the percentage of carbon, hydrogen, and nitrogen. The theoretical and observed values have been comparable with each other. According to the results, around 52–74% of OH groups were replaced by *N*-heterocyclic compounds in PVA. The results are highly correlated with the modification of PVA with acid chlorides.[17] The degree of modification for the polymer **3(a-e)** was found to have 57.5, 72.8, 64.1, 51.6, and 74.3%, respectively. It can be seen that the polymer **3e** has higher degree of modification than all other polymers. The reason may be explained on the basis of pKa value of *N*-heterocyclic compounds, which involved effective reaction with PVA. According to this, **3e** has more pKa value (16.2) and **3d** has lesser value (5.68). This may be the reason towards lesser degree of modification for **3d.** On the basis of the above discussion, the degree of modification of PVA represented as

$$3e > 3b > 3c > 3a > 3d$$

Solubility Analysis

PVA are soluble in hot water and insoluble in most organic solvents. As can be seen from Table II, heterocyclic modified polymers **3(a-e)** were insoluble in water and soluble in polar organic solvents such as pyridine, dimethyl formamide,

dimethyl sulfoxide. The modification drastically changes the solubility behavior of PVA leads to decrease the number of hydroxyl groups contributing to strong inter and intra-molecular hydrogen bonding. The organosolubility of modified PVA also suggested an improvement in processing and further chemical modification.

Swelling Studies

The selected PVA for the present study possesses a weight-average molecular weight of 14,000 and has a degree of hydrolysis of 98–99%. The presence of a large number of hydroxyl groups in the selected polymer results in extensive hydrogen bonding. However, the modified PVA dissolves in hot water owing to the disappearance of such physical bonding at higher temperature. After modification of PVA, hydrolyzed polymer weakens the hydrogen bonding results in a loss of polar nature of the compound and becomes solubility of the polymer in water decreases. A complete swelling study of all heterocyclic modified PVA was carried out at room temperature. Percentage of swelling for the modified PVA **3(a-e)** in water was measured as 121, 241, 80, 26, and 190%, respectively. This is because of heterocyclic compound reacted with the hydroxyl groups of PVA chains and these results in inter and intra molecular type phosphonate ester linkages formed among them. Triazine modified PVA (**3b**) films with water penetrates throughout the interstices of the polymer and results more percentage of swelling behavior. However, a decrease of hydroxyl groups reduce the affinity of the polymers with water and hence swelling percentage was reduced which was observed in piperazine and piperidine modified PVA (**3c, 3d**).

Thermal Analysis

Thermogravimetric analysis (TGA) is used to get information on thermal stability of the polymers **3(a-e)**. The peak temperature, char residue, LOI, T_g, and T_m of all polymers were listed in Table III.

From the TGA measurements (Figure 2), initial thermal degradation temperature (T_{on}) of PVA occurs at 240°C, which may be higher than the modified PVA **3 (a,b)** and lower than the modified PVA **3(c–e)**. For pure PVA, 5–10% weight loss was occurred for water splitting off the polymer chain with the formation of polyene structure.[18,19] The loss of water was also observed for all heterocyclic modified polymers **3(a-e)** because of having few percentages of vinyl alcohol (degree of

Table II. Solubility^a of PVA Before and After Modification

Solvent	PVA	3a	3b	3c	3d	3e
Acetone	X	X	X	X	X	X
Tetrahydrofuran	X	X	X	X	X	X
Methanol	X	X	X	X	X	X
Toluene	X	X	X	X	X	X
Pyridine	X	O	O	O	O	O
Dimethylformamide	X	O	O	O	O	O
Dimethylsulfoxide	Θ	O	O	O	O	O
Water	Θ	X	X	X	X	X

^{a}Three milligram of polymer in 4 mL of water and observed the solubility after 5 h.O, soluble; X, insoluble; Θ, soluble at 70°C.

Table III. Thermal Analysis Data of Modified Polymers

Polymers	T_{on} (°C)	T_{max} (°C)	Char residue (%)			LOI	Tg	Tm
			500°C	600°C	700°C			
PVA	240	487	21.2	0	0	17.5	90	185
3a	221	528	10.0	7.7	7.9	20.6	96.9	233
3b	219	489	16.4	15.2	15.2	23.6	126	183
3c	297	538	17.8	14.1	13.2	22.8	96.9	205
3d	335	490	20.3	20.1	19.8	25.4	95.8	132
3e	269	507	15.5	14.4	14.4	23.3	204	293

T_{on}, Onset thermal decomposition temperature; T_{max}, Maximum thermal decomposition temperature; LOI, limiting oxygen index; T_g, glass transition temperature; T_m, melting temperature.

modification attained only 52–74% found from elemental analysis). Initial thermal degradation temperature for imidazole and triazole modified PVA (**3a,3b**) have been observed at around 221°C and other heterocyclic groups such as piperidine, indole modified PVA (**3c,3e**) found at 297, 269°C, respectively. But in the case of piperazine modified PVA (**3d**) has highest thermal decomposition temperature at 335°C. The reason for such enhancement may be presence of four vinyl linkages attached into piperazine bonded phosphorus moieties. On the basis of the TGA results, order of decreasing thermal stability of the modified polymer is given below:

$$3d > 3c > 3e > PVA > 3a > 3b$$

After the initial thermal decomposition, scission of carbon–carbon bonds occurred in heterocyclic modified polymers and reached the maximum decomposition at about 489–538°C. But, the rate of decomposition was lowered. The same phenomenon was also observed in other phosphorylated PVA and was correlated to the formation of thermally stable phosphorus rich compounds.[20] Liu and Tsai also supported that the phosphorylated PVA exhibited an additional stage of weight loss before

the decomposition of PVA backbones. This is because of phosphorus group attached in the polymer chain. However, this weight loss was not observed for the modified PVA **3(a-e)** because of the high thermal stability of the heterocyclic and phosphorus group.[11]

The LOI value of modified and unmodified PVA has been listed in Table III. According to this, N-heterocyclic modified PVA **3(a-e)** was observed as 20.6, 23.6, 22.8, 25.4, and 23.3, whereas unmodified PVA was 17.5, which implies that all heterocyclic modified PVA has good flame retardance than unmodified PVA. This behavior was mainly due to the presence of P-N, P-C bonds, and heterocyclic compounds in the modified polymers. These structures act as weak links and they were highly susceptible to chain scission during thermal degradation.[21] The LOI values of all heterocyclic modified polymers were comparable with each other. However, polymer **3d** has excellent flame retardance (~ 31% than PVA) character. The increased property of **3d** may be due to the presence of two N—P bonds (increases the overall flame retardancy) than other polymers. Hence, order of decreasing the flame retardancy is listed as follows:

$$3d > 3b > 3e > 3c > 3a > PVA$$

A DSC studies have been carried out a heating rate at 10°C/min (Table III). The glass transition temperature (T_g) of heterocyclic modified polymers **3(a-e)** were found to be 96.9, 126, 96.9, 95.8, 204°C. The observed glass transition temperature value of modified polymers **3(a-e)** were greater than that of pure PVA (90°C). For any pure polymer T_g depends on its chain rigidity, but for a crosslinked polymer it depends on the crosslink density as well as on the chemical structure of the crosslinking agent.[22] The rigidity of the pure PVA is mainly because of the formation of hydrogen bond among the hydroxyl groups of different PVA chains. As soon as a foreign material is introduced in the polymer, it interferes with the hydrogen-bond formation by reaction itself with the hydroxyl groups. This may result in a decrease in the hydrogen-bond interaction, which may reduce the rigidity of the chains; hence T_g is expected to be affected. In the present investigation, T_g value was increased for modified polymers, which may be due to the presence of phosphonyl ester linkages between PVA chains. It was observed from the following decreasing order of glass transition temperature.

Figure 2. TGA thermogram of N-heterocyclic modified PVA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
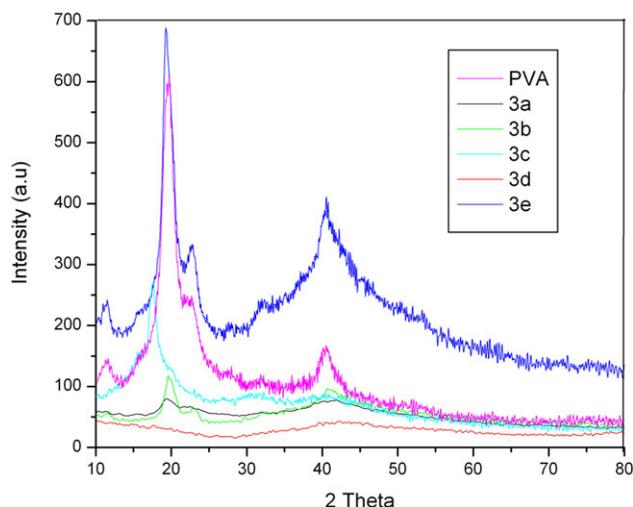
Figure 3. XRD diffractogram of PVA and heterocyclic modified PVA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$3e > 3b > 3a = 3c > 3e > PVA$$

PVA is a semicrystalline polymer, which changes its structure after the crosslinking reaction. Using DSC, the fusion of heating curve can detect from the changes in the melting temperature of the modified polymer. The melting endothermic peak can be seen at 185°C for the pure PVA and after modification with heterocyclic group the melting temperature shifted to 233, 183,

205, 132, and 293°C for **3(a-e)**, respectively. It may be pointed out from the results; melting point temperature was increased for the polymer **3a, 3c, 3e,** and decreased for modified polymer **3b and 3d,** respectively. The reason may be due to the versatile melting point nature of the parent heterocyclic compound attached in the PVA. On the basis of the results, the decreasing order of melting point temperature is given below.

$$3e > 3a > 3c > PVA > 3b > 3d$$

XRD Analysis

X-ray diffractograms of both PVA and heterocyclic modified PVA were shown in Figure 3. It is observed that the intensity of the peak at 19.6° (2θ) in PVA, which is decreased after functionalization with five and six membered heterocyclic compounds. This observation indicates that the modified PVA films are amorphous nature.

AFM Analysis

AFM is a powerful surface technique that can be used to obtain high-resolution images of the surface of organic film.[23] Taking into consideration, the size and shape of the AFM tip, the vertical resolution of AFM images are much better than that of lateral resolution. The obtained diameters usually need to be corrected due to the AFM tip broadening effect.[24] The basic principle involves scanning across a surface when a sharpened probe tip attached to the flexible cantilever tip in tapping mode. Figure 4 shows the AFM images of PVA and heterocyclic modified PVA **3(a-e)** films were formed on silicon substrate using spin coating method. All the films are composed of different heterocycles but exhibit quite different particle size and particle aggregation
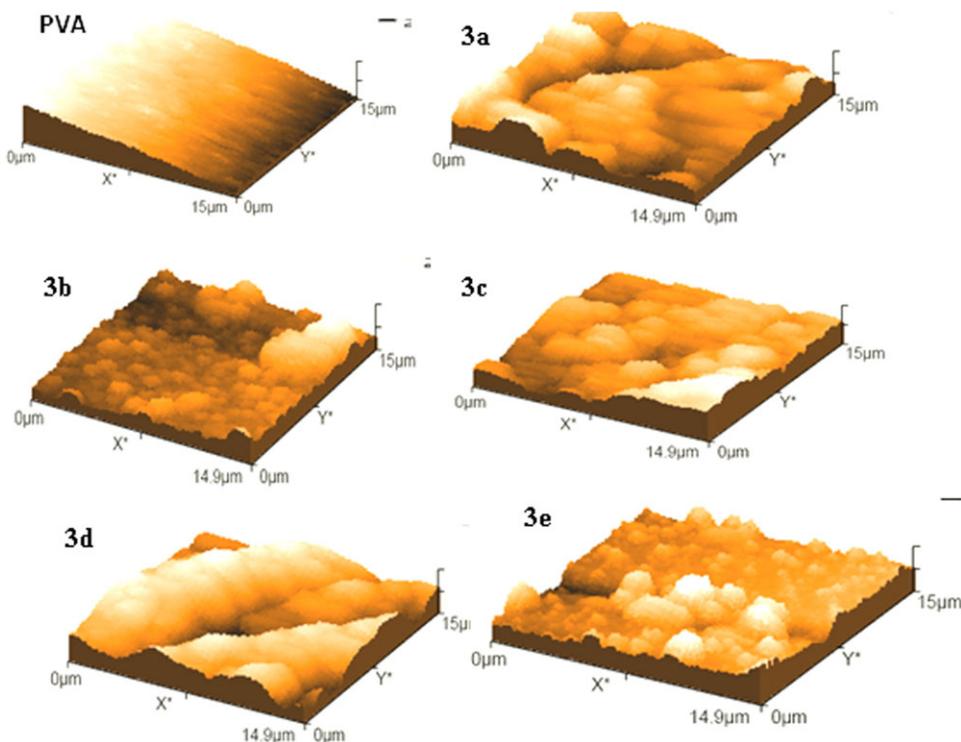
Figure 4. AFM images of PVA and heterocyclic modified PVA **3(a-e)**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table IV. Results of PVA and Modified PVA from AFM Experiments

Polymers	Average surface roughness (Sa) (nm)	RMS roughness (Sq) (nm)	Peak-peak height (Sy) (μm)	Maximum Peak height (Sp) (nm)	Maximum peak valley depth (Sv) (nm)	Mean value (Sa) (nm)	Maximum peak valley (Sp − Sv) (μm)
PVA	10	13	0.12	73	−43	10	0.11
3a	110	150	1	500	−510	110	1.01
3b	83	110	0.88	470	−410	83	0.88
3c	140	180	1.2	460	−700	140	1.16
3d	320	380	0.68	440	−240	46	1.82
3e	46	70	1.8	830	−990	320	0.68

structure. Table IV shows the results of maximum peak valley (**Sp-Sv**), Root mean square (RMS) roughness (**Sq**), and average surface roughness (**Sa**) of the polymer films. These values were obtained from the image analysis tool built in the nanoscope AFM software. It may be seen from the Table IV, the heterocyclic modified PVA shows the peak valley values nearly 10%, 0.8%, 11.6%, 18.2%, and 0.684% higher than the unmodified PVA. Similarly, RMS roughness of modified PVA increases around 10% than pure PVA except the polymer (**3d**). The surface of piperazine functionalized PVA (**3d**) is the roughest (380 nm) and fresh PVA is the smoothest (13 nm). The peculiar properties of **3d** might be due to the increased percentage of vinyl groups which alters its bulkyness. Hence, the increasing order of surface roughness (RMS) of the polymers were listed as

PVA < 3e < 3b < 3a < 3c < 3d

The values of RMS roughness for nitrogen heterocyclic modified PVA was higher than the chemical and heat treated PVA (1.4–6.6 nm)[25] Liang et al., also supported that the roughness of the crosslinked PVA was always higher than that of the fresh PVA at any polymer concentrations.[26]

Adsorption Studies

Figure 5 shows the adsorption capacity of heavy metal ions [i.e., Cu(II), Hg (II), Ni(II), Pb(II), Cd(II), Cr(II), Zn(II), Fe(III)] on the heterocyclic modified PVA. The modified PVA (**3a, 3c, 3d, 3e**) showed high adsorption capacities for Cd(II), Cu(II), Pb(II), Hg(II) than that of Zn (II), Cr(II), Fe(III), Ni(II). The experimental results revealed that the various nature of heterocycle in modified PVA which is easily to bind with the soft metal ions. Similar results were noticed from the cibacron blue F3GA attached PVA.[27]

As can be seen, the order of adsorption of the different heterocylic groups in polymer is as follows:

Imidazole > Piperidine > Piperazine > Indole > Triazole.
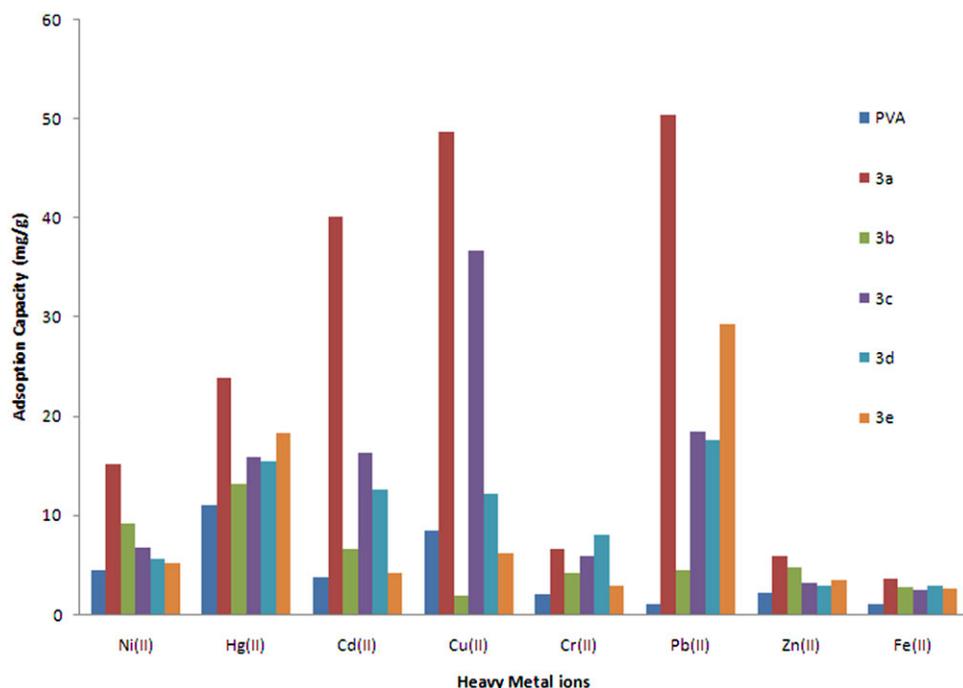
Figure 5. Adsorption capacities of heavy metal ions on the heterocyclic modified PVA **3(a-e)**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
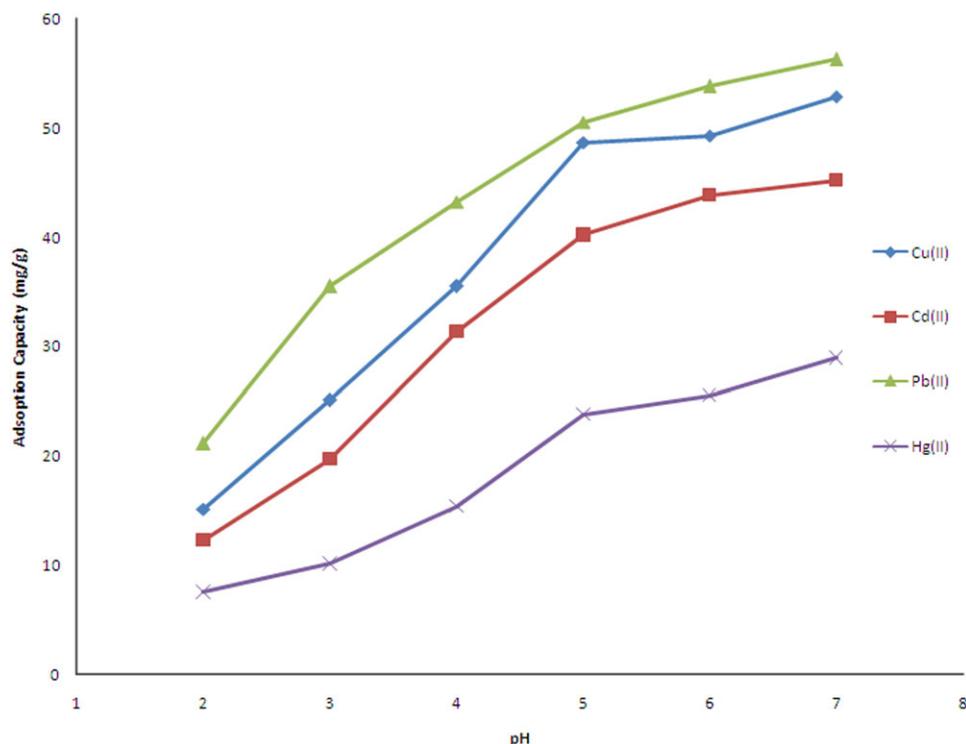
Figure 6. Effect of pH on adsorption of heavy metals on the imidazole modified PVA (**3a**). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Among these, the imidazole modified PVA (**3a**) has the highest adsorption capacity, due to its low hydrophobicity.

The adsorption capacity value for Pb is 289 mg/g of the polymer (**3a**), which is equal to the reported poly(ethylene imine)-PVA matrix system.[28] On comparing the polymers (**3a-3d**), the imidazole functionalized PVA (**3a**) has higher adsorption capacities towards Cd(II), Cu(II), Pb(II), Hg(II) ions, which indicates the length of the hydrophilic spacer arm with nitrogen has the important effect on the adsorption capacity, because the reaction between the functional groups and metal ion is effected by the diffusion of the metal ion into the polymer, the high hydrophobicity of polymer makes the metal ions to interact with the functional groups of the polymers difficulty. Introduction of hydrophilic spacer arm can enhance the hydrophilicity of the ligand and so increase the capacity of polymer.[29]

Effect of pH. Figure 6 shows the effect of pH on Cd (II), Cu(II), Pb(II), Hg(II) adsorption by modified PVA (**3a**). It indicates that the adsorption capacity for the metal ions increased significantly with increase in pH. The results might mainly due to the presence of two nitrogen atoms in imidazole moiety in the polymer (**3a**). At low pH values, i.e., pH < 4.0, the adsorption capacities are lower for all heavy metal ions. The difference in adsorption behavior of Pb(II) as compared to Cd(II), Cu(II), Hg(II) can be explained by the different affinity of the heavy metal ions for the donor atoms in the imidazole moiety. Moreover, the adsorption ability also would decrease because the nitrogen atom of imidazole does not easily forms coordinate bonds with metal ions at low pH. Heterocyclic modified PVA

exhibits the following metal ion selectivity sequence under various pH conditions;

$$Pb(II) > Cu(II) > Cd(II) > Hg(II)$$

CONCLUSIONS

Five types of *N*-heterocycle with phosphorus compounds were synthesized and used to modify the hydroxyl functionality of PVA. Formation of the final compounds was confirmed by using UV, FTIR, NMR, HRMS, and elemental analysis. The degree of modification of the modified PVA was investigated using elemental analysis, which was in the range of 52–74%. Improvement of solubility with organic solvents was also found for PVA before and after incorporation of heterocyclic phosphonyl compound. TGA and DSC thermograms revealed that the modified polymers had good thermal stability than the pure PVA. TGA curves were also analyzed to provide an identification of flame retardance using char yields, which is directly proportional to the LOI. DSC measurements showed an increase in melting temperature and glass transition temperature of the PVA after modification. AFM images presented that the PVA surface possesses nanometer sized roughness and after modification surface roughness increased up to micrometer level. The new modified PVA is found promising for adsorption of Cu(II), Hg (II), Ni(II), Pb(II), Cd(II), Cr(II), Zn(II), and Fe(III) at pH 2.0–7.0. The adsorption capacity of the modified PVA was found to have maximum for Pd (II) (289 mg/g) and minimum for Hg (II) (11 mg/g).

On the basis of the experimental results, heterocyclic modified PVA had good thermal stability, surface roughness, and heavy

metal ion adsorption activity, which may be recommended as a good candidate for environmental application.

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