# Applied Polymer

### Preparation of hydrogel impregnated antimicrobial polyurethane foam for absorption of radionuclide contaminated blood and biological fluids

Avneet Kaur,<sup>1</sup> Sruti Chattopadhyay,<sup>1</sup> Swati Jain,<sup>2</sup> Amit Tyagi,<sup>3</sup> Harpal Singh<sup>1</sup>

<sup>1</sup>Centre for Biomedical Engineering, Indian Institute of Technology Delhi, New Delhi, India

<sup>2</sup>Amity Institute of Nanotechnology, Amity University, Noida, Uttar Pradesh, India

<sup>3</sup>Division of Nuclear Medicine, Institute of Nuclear Medicine & Allied Sciences, Defence R&D Organization, New Delhi 110 054, India

Correspondence to: H. Singh (E-mail: harpal2000@yahoo.com)

**ABSTRACT**: Multi-purpose polyacrylamide (PAM) and polyacrylamide-*co*-sodiumpolyacrylate (PAM-*co*-NaPA) impregnated polyurethane foams (PUF) loaded with iodine have been prepared by *in situ* free radical polymerization. The prepared hydrogel networks displayed higher capacity for absorbing biological fluids as compared to regular PUF sheets and cotton matrices used in hospitals for maintaining hygiene conditions in cases of blood spillage and leakages. PAM-impregnated-PUF showed 910, 605, and 172% absorption in water, saline, and blood, respectively, whereas PAM-*co*-NaPA-impregnated-PUF showed absorption of 1545, 1395, and 269% in water, saline, and blood, respectively in 24 h. Exposure to nuclear, biological, and chemical (NBC) environment has become a grave predicament in today's world necessitating prevention of radiological contaminations especially in medical facilities. PAM-*co*-NaPA-impregnated-PUF displayed 97% absorption of Tc<sup>99</sup> from whole blood whereas PUF sheets were highly hydrophobic and showed only 1% absorption of Tc<sup>99</sup> from whole blood. It was also demonstrated that modified foams have long-term broad-spectrum antimicrobial properties due to sustain release of ionic iodine. Thus, PAM-co-NaPA-impregnated-PUF sheets have strong potential to be used as matrices for carrying the injured patients, from field conditions to hospitals expose to NBC environment. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43625.

**KEYWORDS:** adsorption; biomedical applications; biomaterials; copolymers; foams

Received 25 November 2015; accepted 11 March 2016 DOI: 10.1002/app.43625

#### INTRODUCTION

Cellulosic materials and cotton sheets are used for carrying injured patient from field conditions to hospitals but these matrices suffer from limitations of low absorption and retention of biological fluids and also have no affinity for absorbing radionuclide contaminants. Moreover, they also have higher chances of microbial attack leading to grave postoperative infections.<sup>1</sup> Commercially available hydrogels, capable of absorbing aqueous solutions, are in practice for hygiene articles like diapers, tampons, incontinence products or sanitary napkins. These superbabsorbent resins are crosslinked polymeric hydrogel systems that can swell upto thousand times their own weight in aqueous media and can retain the absorbed liquid under pressure or load.<sup>2,3</sup> Many copolymeric super-absorbing anionic hydrogels have been reported as effective drug delivery carriers owing to their high absorption capacity.<sup>4-6</sup> Sun et al. have synthesized alginate and polyacrylamide hydrogels by creating ionic and covalent crosslinks between their structures. These hydrogels are stretched beyond 20 times their initial length owing to its slide ring structure, which preserves memory of the initial state avoiding large deformations.<sup>7</sup> Many modified polymeric dressings are reported in literature having antibacterial property owing to addition of antibiotic drugs, silver solutions, and nanoparticles.<sup>8–11</sup>

Significant rise in radiological contamination from intentional (nuclear war, terrorism, criminal offence) or unintentional (natural disasters or industrial accidents) ways has also prompted the researchers for development of protection technologies for homeland security and medical facilities.<sup>12,13</sup> Composite polymeric-inorganic absorbers represent a major class of inorganic ion-exchangers for removing heavy metals and isotopes from liquid radioactive wastes.14-16 High radionuclide binding capabilities of modified polyacrylonitrile has been reported for preparing composite absorbent beads for treating acidic and alkaline wastes from U.S. Department of Energy facilities.<sup>17,18</sup> Recently, macro-porous crosslinked poly(glycidyl methacrylateco-ethylene glycol dimethacrylate) copolymers have been synthesized by suspension polymerization and functionalized with diethylene triamine for chemically removing pertechnate ions from aqueous medium.<sup>19</sup> Radioactive decontamination is

© 2016 Wiley Periodicals, Inc.



WWW.MATERIALSVIEWS.COM

particularly pertinent in removing radionuclide from biological fluids such as blood during military operations to prevent further hazards. Nuclear accident or malicious attacks create biohazardous scene with blood spillages, necessitating remediation, and clean up procedures while carrying injured and bleeding patients.<sup>20,21</sup> However, there is no product available in market which can be used as matrices for carrying injured patients from field conditions to hospitals to effectively absorb radionuclide contaminated biological fluids along with good mechanical and antimicrobial properties.

In the present work, we have synthesized iodine loaded polyacrylamide hydrogel impregnated PUF matrices. We have also investigated their absorption capacity with the possible removal of radioactive isotope along with blood and biological fluids. These matrices are further investigated for potential antibacterial activities to curtail subsequent contaminations and potential infections.

#### EXPERIMENTAL

#### Materials

PUF sheet was purchased from Infocom Network Limited, Okhla Industrial Area, New Delhi, India. Acrylamide (AM), methylene bis-acrylamide (MBA) and N,N,N',N'-tetramethyl ethylenediamine (TEMED) were obtained from Sigma Aldrich (USA). Redox free-radical initiator ammonium persulphate (APS) of AR grade quality (99% purity) and elemental iodine was purchased from CDH Chemicals (Mumbai, India). Medical grade Tc99 was obtained from Institute of Nuclear Medicine & Allied Sciences (INMAS), a laboratory of Defence Research and Development Organization (DRDO), Delhi, India. Gamma scintigraphy experiments were carried out under controlled conditions at INMAS under protected environment and the study was approved by its ethical committe. Whole blood was obtained from animal house of INMAS, Delhi. Bacterial strains Escherichia coli and Staphylococcus aureus were obtained from Department of Biotechnology, IIT Delhi (New Delhi, India) for antimicrobial studies. Deionized Milli-Q water (18.2 M  $\Omega$  cm<sup>-1</sup> conductivity) obtained from Millipore Inc., USA, was used in all studies.

#### Methods

Synthesis of Polymeric Hydrogel Impregnated PUF Sheets. Polymeric hydrogels impregnated PUF sheets were synthesized by simultaneous in situ free radical polymerization of acrylamide (AM) with methylene-bis-acrylamide (MBA) as crosslinker inside porous polyurethane foam (PUF). AM (5.2 g) were dissolved in 18 mL distilled water in 250-mL beaker under nitrogen atmosphere to maintain oxygen free environment, followed by addition of crosslinker MBA (0.0416 g and 0.104 g) initiator APS (0.39 g) and promoter TEMED (0.015 g) with constant stirring. PUF sheet  $(40 \times 40 \times 15 \text{ mm})$  was immediately dipped into the solution to allow absorption of monomer solution into PUF and placed in incubator shaker at 37 °C for 6 h to get polyacrylamide (PAM) impregnated PUF sheet.<sup>22</sup> Washing was done by dipping the PAM-impregnated-PUF sheet samples into warm water three to five times until no optical density of residual monomer was observed in washed water at 260 nm under UV visible spectroscopy. Different polymeric



**Scheme 1.** Schematic representation of polymeric hydrogel impregnated PUF. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

hydrogel impregnated PUF samples were prepared by varying the percentage of MBA crosslinker (0.8 and 2%). Polymeric hydrogel impregnated PUF sheets were dried in vacuum oven to a constant mass and finally stored in dessicator till further use. PAM was hydrolyzed to sodiumpolyacrylate by dipping the modified foam in 0.5N sodium hydroxide solution at 70-80 °C for 3 h, followed by washing and then dried in vacuum oven at 60-70 °C for 24 h and the product is designated as PAM-co-NaPA-impregnated-PUF. The iodination of polymeric hydrogel impregnated PUF samples was accomplished by dipping them into the molecular iodine (10% and 20% based on polymer weight) solution in 20 mL of dichloromethane for 24 h, then washed several times with Milli-Q water to remove traces of free iodine, if present and dried in dark for 8 h at room temperature and the resulting product is referred as iodinated polymeric hydrogel impregnated PUF samples. Simultaneous aqueous bulk polymerization of PAM with 0.8% of MBA was also carried out in 50-mL beaker under similar conditions and polymer thus obtained was dried and crushed into powder.

**Degree of Hydrolysis in Polymeric Hydrogel Samples.** Totally, 0.1 g of PAM and PAM-*co*-NaPA hydrogel samples were taken separately in 250 mL beaker containing 20 mL of 0.1 N hydrochloric acid solution with 10 ml of distilled water, kept at room temperature for 24 h with continuous stirring and then titrated with 0.1 N solution of potassium hydroxide, using phenolphthalein as an indicator to calculate the mg of KOH used per gram of sample.

**Characterization of Polymeric Hydrogel Samples.** Synthesized polymeric hydrogel samples were characterized for different functional groups by Attenuated Total Reflectance–Fourier Transform infrared (ATR-FTIR) spectroscopy measurements using Perkin Elmer Spectrum One spectrometer, USA. Surface morphology was examined through STEREOSCAN 360 Cambridge Scanning electron microscope (Cambridge Scientific Industries Limited, England) by mounting the polymeric hydrogel impregnated PUF samples on a metallic stub using double-



WWW.MATERIALSVIEWS.COM



Figure 1. Synthesis of PAM-co-NaPA.

sided carbon tape with silver paint. Gold sputtering was done by sputtering instrument (BioRad Polaran Sputter, Model 50X) on specimen stub to incur conductivity in samples for improving resolution. Stability of polymeric hydrogels was obtained by X-ray diffractometer (Philips X'Pert PRO Thin Film X-ray Diffractometer) at wavelength Cu-K<sub> $\alpha$ </sub> = 1.54 Å operating at a voltage of 45 kV and a current of 40 mA at the rate of 2°/min in the range of diffraction angel 20-80°  $\theta$ . Thermal properties of polymeric hydrogel samples were determined by differential scanning calorimetry on DSC-6 module of Perkin Elmer delta series thermal analyzer. All the studies were carried out at a heating rate of 10 °C/min from 30 °C to 250 °C in nitrogen atmosphere. The mechanical properties of PUF samples were determined in dry and swollen state by using Instron Universal Testing Machine, USA at room temperature. Samples were placed on top of compression load plate and pressed by a cylinder-shaped metal disc with a strain rate of 25 mm/min. Tensile as well as compression strength of PUF samples was performed according to ASTM D3574-11 standard.<sup>23</sup> Average value of five test samples was noted. Release behavior of iodinated polymeric hydrogel impregnated PUF samples were measured by ion-selective electrode (ISE) at room temperature.

Pre-weighed small pieces of polymeric hydrogel impregnated PUF samples were immersed in distilled water and saline and were weighed at specific time after wiping adsorbed fluid from the surface. Swelling characteristics of polymeric hydrogel impregnated PUF samples in water and saline was determined by calculating the percentage through the following equation.

% Swelling = Weight of swollen sample – Weight of dry sample Weight of dry sample ×100 Sterilization studies were carried-out by the standard method of autoclaving with 121 °C temperature at 15 lbs pressure for 20 min. Flammability studies of different PUF samples were studied by performing horizontal burning test as per UL-94.<sup>24</sup> Natural gas was applied to one end of the specimen samples, horizontally held by metallic tonks to allow burning from one reference pint point till other mark. Time was measured for the flame to reach the second marked point and an average value of three samples was noted.

**Fluid Holding Behavior.** The water, saline and blood holding capacity of polymeric hydrogel impregnated PUF samples under continuous and static flow conditions were measured.<sup>25</sup> Continuous flow of liquids including water and saline was maintained from Louis pasture volumetric burette at 30–32 and 50–52 drops/min to evaluate the rate of fluid absorption by different polymeric hydrogel impregnated PUF sheets ( $40 \times 40 \times 15$  mm). In another approach hydrogel impregnated PUF samples ( $5 \times 5 \times 5$  mm) were incubated with 50 mL of different fluids (water, saline, and blood) to allow their absorption for 24 h and the percentage swelling of each sample was measured. All experiments were performed in triplicate for each sample and the average value were reported.

Sorption of Radionuclide from Biological Fluids. Biologically relevant fluid (blood) was mixed with the Technetium-99 (Tc99) by the standard procedure developed by INMAS, New Delhi. 0.05-mille curie (mci) of Tc99 was slowly added to 1 mL of blood and homogenized with continuous stirring in properly maintained conditions to prepare radioactive stock solutions. Further, radioactive stock solution was added dropwise onto the polymeric hydrogel impregnated PUF samples ( $5 \times 5 \times 5$  mm) at a rate of 14–16 drops/min till spillage. Gamma camera with

Table	L	Swelling	Percentage	of Pol	vmeric F	Hydrogel	Impregnated	PUF	Samples
Table	1.	Swennig	reneemage	01 1 01	ymene i	Tyuroger	impregnateu	101	Samples

Sample no.	PUF samples	Crosslinking agent MBA (%)	Swelling percentage in water (24 h)	Swelling percentage in water (10 days)
1	PAM-impregnated-PUF	0.8	$522 \pm 3$	$569 \pm 4$
2	PAM-co-NaPA-impregnated-PUF	0.8	$625 \pm 4$	$1397 \pm 5$
3	PAM-impregnated-PUF	2	$528 \pm 3$	528±3
4	PAM-co-NaPA-impregnated-PUF	2	$835 \pm 4$	$835 \pm 4$





Figure 2. ATR-FTIR spectroscopic studies of (a) PAM and (b) PAM-co-NaPA.

gamma counter was used to count the radioactivity with the help of dedicated software. All experiments were carried out in triplicate and an average value was recorded. Percentage relative measurements of sorbed radioactivity were obtained using following the equation:

$$\frac{\% \text{ Sorbed } Tc^{99} = \text{ Sorbed } Tc^{99} \text{ counts in PUF samples}}{\text{Sorbed } Tc^{99} \text{ in stock solution}} \times 100$$

Antimicrobial Assessment. Antimicrobial activities of iodinated polymeric hydrogel impregnated PUF samples were done in two steps by quantitatively assessing iodide ions release pattern and then studying their potential bacteria mitigation properties. Iodinated polymeric hydrogel impregnated PUF samples (5 × 5 × 5mm) were used for release study of iodine in 50 mL Milli-Q water for 24 h and then replaced with fresh water after every 24 h. Ionic iodine concentrations in water samples were measured using ion-selective electrode upto 15 days. Antimicrobial efficacy was tested against known concentration of bacterial strains (*E. coli* and *S. aureus*, 1 × 10<sup>4</sup>). A lawn of bacterial

strain was laid onto the nutrient agar plate using sterile spreader. Then iodinated polymeric hydrogel impregnated PUF samples were placed in each plate and incubated for 37 °C for 24 h and the clear zone of inhibition around the sample was measured.

#### **RESULTS AND DISCUSSION**

The present study is directed towards the preparation of hydrogel impregnated PUF sheet capable of absorbing radionuclide contaminated blood and biological fluids. PUF sheets are hydrophobic, soft, and flexible synthetic sponge with optimal mechanical strength and abrasion resistance and are commonly used as a bedding material.<sup>26</sup> However, these matrixes have no affinity for blood and biological fluids absorption due to their hydrophobic nature and are not ideal for carrying injured patients from field conditions to hospitals exposed to NBC environment. Polymeric hydrogel impregnated PUF samples were successfully prepared (Scheme 1, Figure 1) by in situ free radical polymerization of acrylamide containing various percentage of MBA as crosslinker (Table I) inside the PUF using APS and TEMED as redox initiator at room temperature. We prepared polyacrylamide using 0.8% and 2% crosslinker during preliminary studies however we abundant the 2% crosslinker based formulation due to its less swelling and brittle nature. Amide functionalities were further hydrolyzed to carboxylic groups using dilute sodium hydroxide solution at temperature of 70-80 °C.<sup>27-29</sup> PAM showed acid value of less than 5mg KOH/g whereas PAM-co-NaPA showed the acid value of 220 mg KOH/g confirming the partial conversion of polyacrylamide to carboxylate groups.

#### ATR-FTIR Studies

ATR-FTIR Spectra of polymeric hydrogel samples are given in Figure 2. PAM showed regular peaks at 3180 cm<sup>-1</sup>, 1600 cm<sup>-1</sup>, and 1410 cm<sup>-1</sup>, due to N–H, O–C–O– stretching vibrations and –C–H bending vibration of amide groups confirming the





(c) PAM-co-NaPA-impregnated-PUF

Figure 3. Scanning electron micrographs of (a) PUF (b) PAM-impregnated-PUF and (c) PAM-*co*-NaPA-impregnated-PUF. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]





Figure 4. X-ray diffractogram of (a) PAM (b) PAM-co-NaPA.

presence of amide functionality. PAM-*co*-NaPA showed peaks at 3180 cm<sup>-1</sup> due to stretching of N—H and O—H and peak at 1400 cm<sup>-1</sup> due to —C—H bending. Spectra of PAM-*co*-NaPA showed a broad band at 1660 cm<sup>-1</sup> (C=O stretching) due to formation of carboxylic groups confirming the presence of polyacrylic acid in PAM-*co*-NaPA. FTIR spectral analysis is indicative of the formation of hydrogel and its subsequent hydrolysis under alkaline conditions.<sup>30</sup>

#### Scanning Electron Microscopy

SEM images of polymeric hydrogel impregnated PUF samples are given in Figure 3. The cross-sectional view of PUF presents a highly irregular surface with mesoporous structure. Impregnation of PAM/PAM-*co*-NaPA polymer decreased the porosity of native PUF illustrating easy penetration of monomer to create hydrogel inside its porous network. On alkaline hydrolysis, morphology of PAM-*co*-NaPA-impregnated-PUF further changes due to excessive swelling of PAM-*co*-NaPA as compared to PAM.

#### **X-ray Diffraction**

XRD diffractogram of polymeric hydrogel samples are given in Figure 4. The diffractogram of PAM showed mild crystalline

structure with one characteristic peak at  $2\theta = 30^{\circ}$  whereas PAM-*co*-NaPA showed a crystalline structure with characteristics peaks at  $2\theta = 30^{\circ}$ ,  $36^{\circ}$ ,  $40^{\circ}$ ,  $43^{\circ}$ ,  $48^{\circ}$ , and  $49^{\circ}$  due to hydrolysis of PAM to polyacrylic acid,<sup>31</sup> Anionic charges due to carboxylic groups result in alignment of polymeric chains and thus crystal-linity observed due to repulsion between negative charges. Similar results have also been reported in the literature.<sup>32</sup>

#### Thermal Analysis

Thermal behavior of polymeric hydrogel samples was studied by differential scanning calorimetry (DSC) to examine the glass transition temperature. DSC heating thermograms of polymeric hydrogel samples are shown in Figure 5. PU foam is flexible with the  $T_g$  value of 45 °C.<sup>33</sup>  $T_g$  value increased to 122 °C and 113 °C on incorporation of PAM and PAM-*co*-NaPA, respectively due to their brittle nature in dry state but became flexible on absorption of water and biological fluids.

#### Sterilization and Inflammability studies

PAM-impregnated-PUF and PAM-co-NaPA-impregnated-PUF samples were found to withstand sterilization conditions (121 °C temperature at 15 lbs pressure for 20 min of time). No morphological, analytical and spectral changes were observed in native and hydrogel modified foam sheet after the sterilization procedure. All PUF systems burned completely to ashe during horizontal flammability test with different rates of burning. The results revealed that PUF burned in shortest time of only 13 s while PAM-impregnated-PUF and PAM-co-NaPA-impregnated-PUF burned in  $\sim$ 300 and 600 s, respectively (Figure 6). All these results confirm that native PUF is highly inflammable and flame resistance improved after the incorporation of PAM/ PAM-co-NaPA hydrogel into PUE.23 Higher burning stability of PAM-co-NaPA-impregnated-PUF is probably because of crosslinking of polymer due to formation of anhydride linkages between polymeric chains containing carboxylic groups.<sup>34–36</sup>



Figure 5. DSC thermograms of (a) PAM and (b) PAM-*co*-NaPA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]

#### **Applied Polymer**



**Figure 6.** Comparison of inflammation time for polymeric hydrogel impregnated PUF samples.

However, it is well known that carboxylic groups containing polymers form crosslink structure on heating due to loss of water and formation of anhydride linkage but there is no report related to improvement in burning stability.

#### **Mechanical Properties**

Compressive and tensile strength of synthesized polymeric hydrogel impregnated PUF samples were evaluated according to ASTM standard D3574-11 in both dry and wet conditions. Negligible change in compressive strength was recorded on introduction of polymeric hydrogel into PUF while the tensile strength reduced to half the original value. Tensile and compressive strength further decreased significantly on hydrolysis of PAM, probably because of high water absorption<sup>37</sup> of PAM-*co*-NaPA-impregnated-PUF compare to PAM-impregnated-PUF [Figure 7(a,b)]. However, on storage PAM-impregnated-PUF sheet become brittle in one month while PAM-*co*-NaPA-impregnated-PUF sheet retain their flexibility due to high affinity for water, which act as a plasticizer.

#### **Swelling Studies**

Swelling percentage of various polymeric hydrogel impregnated PUF samples are given in Table I. It was observed that with increasing crosslinker MBA concentration in hydrogel composition, swelling percentage decreased owing to formation of rigid networks of polymeric chains inside the foam. Polymeric hydro-



Figure 7. Mechanical properties of polymeric hydrogel impregnated PUF samples.



Figure 8. Swelling characteristics of polymeric hydrogel impregnated PUF samples in different medium (water and saline).

gel impregnated PUF samples containing 2% of crosslinker showed less absorption and high rigidity in dry condition while the polymeric hydrogel impregnated PUF samples prepared with 0.8% crosslinker showed higher fluid absorption with good mechanical properties. It was noted that swelling values of PAM-impregnated-PUF samples containing 0.8% of MBA showed 570 and 450% swelling in water and saline which increased to 1399 and 1085% swelling in water and saline for hydrolyzed PAM-co-NaPA-impregnated-PUF (Figure 8). Hydrolysis of PAM generated ionizable carboxylic functionalities, which impart high water swellability to the polymeric hydrogel impregnated PUF samples. It is well known that the swelling of a hydrogel is induced by the electrostatic repulsion of the ionic charges of its network. Coupling high negative charge with low crosslink density gives hydrogel foams the ability to rapidly take water molecules upto 1000% of their own weight.38,39

Hydrolyzed PUF sheet had highest swelling for all relevant biological fluids. However, swelling values of polymeric hydrogel modified PUF samples were always less in saline as compare to aqueous medium probably due to common ion effect of salts.

## Fluid Holding Behavior of Polymeric Hydrogel Impregnated PUF Samples

Results of absorption of water and saline in continuous drip flow condition in water and saline are given in Table II. It was observed that PAM-impregnated-PUF showed 25–27 mL of water absorption without any spillage at a rate of 30–32 drops/ min while water absorption capacity increased to 30–32 ml on hydrolysis of PAM to polyacrylic acid due to ionic nature and

**Table II.** Studies of Fluid Holding Behavior of Polymeric Hydrogel

 Impregnated PUF Samples in Continuous Drip Flow Conditions

PUF Samples		30-32 drops/min (mL)	50-52 drops/min (mL)
PAM-impregnated-PUF	Water	25 ± 2	14 ± 2
	Saline	$17 \pm 2$	$10 \pm 2$
PAM-co-NaPA- impregnated-PUF	Water	30±2	$25\pm2$
	Saline	27 ± 2	$23 \pm 2$

Table I	II. Stu	ıdies	of Fluid	Holding	Behavior	of Polymer	ic Hydrogel
Impreg	nated	PUF	Samples	in Static	Conditio	ons	

	% of swelling in 24 h		
PUF samples	Water	Saline (0.9%)	Blood
PUF	110 ± 2	70 ± 2	9±1
PAM-impregnated-PUF	$910\pm4$	605 ± 2	$172 \pm 2$
PAM-co-NaPA- impregnated-PUF	$1545 \pm 5$	$1395 \pm 4$	269±2



**Figure 9.** Radioactivity images of polymeric hydrogel impregnated PUF samples using Tc99 incorporated blood. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

repulsion between the negative charges on the polymer chains. However, it was also observed that water retention capacity of all hydrogel samples decreased on increasing the flow rate to 50–52 drops/min due to slow interaction of fluids with hydrogel after 30–32 drops/min.

Percentage of fluid holding in polymeric hydrogel impregnated PUF samples under static condition in water, saline and blood are given in Table III. PAM-impregnated-PUF showed 910, 605, and 172% absorption in water, saline, and blood, respectively, whereas PAM-*co*-NaPA-impregnated-PUF showed absorption of 1545, 1395, and 269% in water, saline, and blood, respectively on hydrolysis of PAM to polyacrylic acid. Decrease in swelling



Figure 10. Release studies of iodinated polymeric hydrogel impregnated PUF samples.

percentage in case of saline is probably due to common ion effect of salts. In comparison with aqueous medium, swelling in blood is also retarded for both PAM-impregnated-PUF and PAM-*co*-NaPA-impregnated-PUF due to the presence of salts, large cellular components, proteins, and other macromolecules that pose difficulty in penetration of fluids in the crosslinked network by building osmotic pressure gradient.

#### Sorption of Tc99

Results of sorption of radio-contaminated (Tc99) blood by various polymeric hydrogel impregnated PUF samples, as measured by Gamma scintigraphy, are presented in Figure 9. PUF, PAMimpregnated-PUF & PAM-*co*-NaPA-impregnated-PUF samples showed 1, 49, and 97% absorption of Tc99, respectively. Lowest number of Tc99 counts were obtained from PUF indicating its high hydrophobicity and poor radionuclide absorption ability whereas higher radionuclide absorption in PAM/PAM-*co*-NaPAimpregnated-PUF is probably due to higher water absorption and ionic charges present on them.

Antimicrobial Assessment. Results of the iodine release from various polymeric hydrogel samples in Milli-Q water, are given in Figure 10. Iodinated polymeric hydrogel impregnated PUF (20% Iodine) showed ~686 ppm cumulative ionic iodine release as compared to 356 ppm for 10% iodinated sample. Both samples showed the sustained release of iodide ions till 15 days of study period. Antimicrobial activity of iodinated polymeric hydrogel impregnated PUF samples are given in Table IV. A prominent zone of inhibition was observed around all iodinated polymeric hydrogel impregnated PUF samples against *E. coli* and *S. aureus* confirming their broadspectrum antimicrobial activity. Zone of inhibition (ZOI) increased with increase in loading of iodine in the polymeric hydrogel PUF samples. The released iodide ions bind with various biomolecules present in the cell membrane of microbial cells and thus destroy the cell membrane and inhibit various cell processes.<sup>40,41</sup>

Table IV. Zone of Inhibition (ZOI) of Iodinated Polymeric Hydrogel Impregnated PUF

	Zone of Inhibition (mm)							
Bacterial strains	PAM-impregnated- PUF (10% iodine)	PAM-co-NaPA-impregnated- PUF (10% iodine)	PAM-impregnated- PUF (20% iodine)	PAM-co-NaPA-impregnated- PUF (20% iodine)				
S. aureus	30	30	34	34				
E. coli	32	32	36	36				



#### CONCLUSIONS

Macro-porous polyurethane foam was modified by in-situ free radical polymerization of acrylamide to yield polyacrylamide and further hydrolyzed to yield PAM-co-NaPA-impregnated-PUF. These polymeric hydrogel impregnated foams effectively absorbed water, saline, and blood. The developed PAM-co-NaPA-impregnated-PUF matrices showed high fluid retention capacity without any leakage and spillage of fluids for longer period of time. Hydrogel impregnated PUF matrices have higher water and blood absorption capacity as compared to cotton sheets and matrices currently used in medical operational theater, outpatient facilities and patient transport facilities such as stretchers. Hydrogel impregnated PUF matrices were also evaluated to remove radioactive contaminated biological fluids and results indicated that highest Tc99 absorption capabilities were observed in PAM-co-NaPA-impregnated-PUF followed by PAMimpregnated-PUF from whole blood while PUF sheet showed negligible Tc99 absorption. Our studies also demonstrated that addition of molecular iodine in the hydrogel impregnated PUF matrices efficiently mitigated the microbial contamination by sustained release of ionic iodide species. These developed multifunctional matrices have strong potential to be explored as antimicrobial matrices for mitigation of pathogenic bacteria and absorption of radionuclide contaminated blood and biological fluids for carrying injured patients, from field conditions to hospitals, exposed to NBC environment.

#### ACKNOWLEDGMENTS

Authors would like to acknowledge their financial support from Defence Research Organization (DRDO) (INM/TC/2519/2012), New Delhi, India in carrying out this research work.

#### REFERENCES

- 1. Behrens, A. M.; Sikorski, M. J.; Li, T.; Wu, Z. J.; Griffith, B. P.; Kofinas, P. Acta Biomaterialia **2014**, *10*, 701.
- 2. Ahmed, E. M. J. Adv. Res. 2013, 6, 105.
- Beck, M.; Frenz, V.; Kowalski, A.; Selzer, E.; Bauer, E.; Keller, H.; Steinmetz, B. U.S. Patent, A1, US20070066947 (2007).
- 4. Pandey, M.; Amin, M. C. Neurosci. Therapeutics 2014, 20, 377.
- 5. Omidian, H.; Rocca, J. G.; Park, K. J. Control Release 2005, 102, 3.
- Laftah, W. A.; Hashim, S.; Ibrahim, A. N. Polym.-Plast. Technol. Eng. 2011, 50, 1475.
- Sun, J. Y.; Zhao, X.; Illeperuma, W. R. K.; Chaudhuri, O.; Oh, K. H.; Mooney, D. J.; Vlassak, J. J.; Suo, Z. *Nature* 2012, 489, 133.
- Park, J. K.; Lee, J. H.; Kwak, J. J.; Shin, H. B.; Jung, H. W.; Bae, S. W.; Yeo, E. D.; Lee, Y. K.; Yang, S. S. *Wounds* 2013, 25, 153.
- 9. Bhende, S.; Spangler, D. Infect Control Hosp. Epidemiol. 2004, 25, 664.

- Arce, J. M. S.; Tatay, A. I.; Luna, M. L.; Boix, Y. S.; Deltell, J. G.; Barberá, E. G.; Heras, J. B.; Serrano, M. G. *Cirugía Española* 2011, 89, 532.
- 11. Gupta, B.; Agarwal, R.; Alam, M. S. Indian J. Fiber Text. Res. 2010, 35, 174.
- 12. Feltcorn, E. Environmental Protection Agency U.S. EPA 2006, 402-R-06-003.
- Center for Radiation Site Cleanup, New York City Hazard Mitigation Plan Chemical, Biological, Radiological, and Nuclear (CBRN) 2014, 1–13.
- 14. Aberkane-Mechebbek, L.; Larbi-Youcef, S. F.; Mahlous, M. Mater. Sci. Forum 2009, 609, 255.
- 15. Wang, J.; Li, X. Ind. Eng. Chem. Res. 2013, 52, 572.
- 16. Kawalec, M.; Dove, A. P Mespouille, L.; Duboisa P. Polym. Chem. 2013, 4, 1260.
- 17. Sebesta, F.; John, A.; Motl, A. U.S. DOE Facilities 1995.
- 18. Sebesta, F.; John, J.; Motl, A.; Stamberg, K. Contractor Report 1995, SAND952729.
- Hercigonja, R. V.; Maksin, D. D.; Nastasovic, A. B.; Trifunovic, S. S.; Glodic, P. B.; Onjia, A. E. J. Appl. Polym. Sci. 2012, 123, 1273.
- 20. Holcomb, J. B. Crit. Care 2004, 8, S57.
- Casey, B. J.; Behrens, A. M.; Tsinas, Z. I.; Hess, J. R.; Wu, Z. J.; Griffith, B. P.; Kofinas, P.; Brendan, J. J. Biomater. Sci. Polym. 2013, 24, 1781.
- 22. Oh, S. T.; Kim, W. R.; Kim, S. H.; Cung, Y. C.; Park, J. S. *Fibers Polym.* **2011**, *12*, 159.
- 23. Standard test methods for flexible cellular materials-slab, bonded and molded urethane foams; Designation: D3574-11, ASTM International.
- 24. Gupta, A. K.; Biswal, M.; Mohanty, S.; Nayak, S. K. Adv. Mech. Engg. 2012, 13.
- 25. Alaei, J.; Broojerdi, S. H.; Rabiei, Z. Petroleum Coal 2005, 47, 32.
- 26. Shimamoto, T. J. Cardiothoracic Surg. 2011, 6, 26.
- 27. Rabiee, A.; Zeynali, M. E.; Baharvand, H. Iran. Polym. J. 2005, 14, 603.
- 28. Zhou, C.; Wu, Q. Colloids Surf. B: Biointerfaces 2011, 84, 155.
- 29. Kurenkov, V. F.; Hartan, H. G.; Lobanov, F. I. Russian J. Appl. Chem. 2011, 74, 543.
- Murugan, R.; Mohan, S.; Bigotto, A. J. Korean Phys. Soc. 1998, 32, 505.
- 31. Gohar, M. R. Y.; Kabiri, K.; Mehr, M. J. Z.; Hashemi, S. A. *J. Polym. Res.* **2010**, *17*, 151.
- 32. Rakhshani, M.; Kamrannejad, M. M.; Babaluo, A. K.; Rezaei, M.; Aghjeh, M. R. *Iran. Polym. J.* **2010**, *21*, 821.
- Magalhaes, A. S. G.; Neto, M. P. A.; Bezerra, M. N.; Feitosa, J. J. Brazilian Chem. Soc. 2013, 24, 304.
- Hatakeyama, H.; Hirogaki, A.; Matsumura, A.; Hatakeyama, T. J. Thermal Anal. Calorim. 2013, 114, 1075.
- 35. Saravanan, D.; Gomathiand, T.; Sudha, T. P. N. Arch. Appl. Sci. Res. 2011, 3, 342.

- Morfopoulou, C. I.; Aikaterini, K.; Andreopoulou, A. K.; Daletou, M. K.; Neophytides, S. G.; Kallitsis, J. K. J. Mater. Chem. A 2013, 1, 1613.
- 37. Nagase, K.; Sakaguchi, J. Polym. Sci. Part A 1956, 3, 2475.
- 38. Karadag, E.; Saraydi, D. Turk. J. Chem. 2002, 26, 863.
- 39. Thorn, R. M. S.; Austin, A. J.; Greenman, J.; Wilkins, J. P. G.; Davis, P. J. *J. Wound Care* **2009**, *8*, 343.
- 40. Leaper, D. J.; Durani, P. Int. Wound. J. 2008, 5, 361.
- 41. Dai, T.; Huang, Y. Y.; Sharma, S. K.; Hashmi, J. T.; Kurup, D. B.; Hamblin, M. R. *Antiinfect. Drug Discov.* **2010**, *5*, 124.

