



Hydrogels based on a three component system with potential for leaching metals

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ABSTRACT

In this paper, new biodegradable hydrogels were prepared, characterized and evaluated for metal ions absorption capacity from aqueous systems. The hydrogels are based on reaction of chitosan with polyvinyl alcohol, chitosan and polyvinyl alcohol with glutaraldehyde, N,N'-bisoxmaleimide, and N,N'-bisoxphthalimide under different reaction conditions to give the corresponding hydrogels P-C(I), P-C-G(II), P-C-B (III), and P-C-P(IV). The new hydrogels were characterized by FTIR spectroscopy, thermal stability, morphology, crystallography, solubility and swelling ratio. This preliminary investigation of the metal ion entrapment efficiency of the hydrogels showed that chitosan–polyvinyl alcohol–N,N'-bisoxphthalimide [P-C-P(IV)] hydrogel recovered Cu^{2+} ions with efficiencies reaching 52.5%, and for Co^{2+} ions 72.5% from aqueous solution systems.

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1. Introduction

Chitosan, a copolymer that is primarily composed of (1 → 4) linked 2-amino-2-deoxy-D-glucopyranose units, and residual 2-acetamido-2-deoxy-D-glucopyranose units, is a chemical derivative obtained by alkaline deacetylation of chitin and also it is found naturally in some fungal cell walls. Since it is harmless to humans and presents excellent biological properties such as biodegradation in the human body, immunological, antibacterial, and wound-healing activity (Synowiecki & Al-Khateeb, 2003; Jayakumar, Prabakaran, Reis, & Mano, 2005), chitosan has been widely used in food and pharmaceutical processes and in medical and agricultural drugs (Kifune, 1992; Kawamura, Mitsuhashi, Tanibe, & Yoshida, 1993; Ravi Kumar, 2000; Sashiwa & Aiba, 2004).

Chitosan is well known as an excellent biosorbent for metal cation removal in near-neutral solutions because of the large number of NH_2 groups. The excellent adsorption characteristics of chitosan for heavy metals can be attributed to (1) the high hydrophilicity due to the large number of hydroxyl groups of glucose units, (2) the presence of a large number of functional groups (acetamido, primary amino and/or hydroxyl groups) (3) the high chemical reactivity of these groups and (4) the flexible structure of the polymer chain (Crini, 2005). The reactive amino group selectively binds to virtually all group III transition metal ions but does not bind to groups I and II (alkali and alkaline earth metal ions)

(Muzzarelli, 1973). Also, due to its cationic behavior, in acidic media, the protonation of amine groups leads to adsorption of metal anions by ion exchange (Guibal, 2004; Kunkoro, Roussy, & Guibal, 2005).

Chemical modification of chitosan has two main aims: (a) to improve the metal adsorption properties, and (b) to change the solubility properties of chitosan in water or acidic medium. The chemical substitution reactions involve the NH_2 group in the C2 position and/or the OH groups in the C3 and C6 positions of acetylated and deacetylated units. The main reaction easily performed involving the NH_2 group is the quaternization of the original primary amino group or the secondary amino group obtained after reductive amination after an aldehydic function has reacted with the NH_2 group (Rinaudo, 2006).

PVA is a synthetic water-soluble hydrophilic polymer. The basic properties of PVA are dependent on the degree of polymerization or on the degree of hydrolysis. It has been widely used in adhesives, emulsificants, in the textile and paper industry applications and in the attainment of amphiphilic membranes for enzyme immobilization (Mansur et al., 2000). Most recently, PVA has been used in pharmaceutical and biomedical applications for controlled drug release tests due to its degradable and non-toxic properties (Peppas, Huang, Torres-Lugo, Ward, & Zhang, 2000). Chemical crosslinking is a highly versatile method to create and modify polymers, where properties can be improved, such as mechanical, thermal and chemical stability (Mansur et al., 2000; Mansur & Mansur, 2005).

Polyvinyl alcohol is one of the more widely used polymers because of its excellent mechanical properties. It is also

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biodegradable under suitable conditions (Takasu, Aoki, Tsucyia, & Okada, 1999). Commercial PVA is a mixture of different types of stereoregular PVA structures (isotactic, syndiotactic and atactic).

Glutaraldehyde is used as a cross-linking agent for PVA and some polysaccharides such as heparin, (Rollason & Sefton, 1989) as well as hyaluronic acid and chitosan (Roberts & Taylor, 1989).

Chitosan blends with polyvinyl alcohol are widely discussed (Arvanitoyannis, 1999; Miya, Iwamoto, & Mima, 1983). They are also used in the formation of hydrogels (Koyano, Minoura, & Nagura, 1998) and as membranes (Mucha et al., 2000; Wu, Zhu, & Liu, 1994; Mucha, Ludwiczak, & Kawinska, 2005).

By definition, hydrogels are polymeric networks with a three-dimensional configuration capable of imbibing high amounts of water or biological fluids (Peppas & Mikos, 1986; Brannon-Peppas, 1990; Bouwstra & Jungiger, 1993). Their affinity to absorb water is attributed to the presence of hydrophilic groups such as $-OH$, $-CONH_2$, and $-SO_3H$ in polymers forming hydrogel structures (Peppas & Khare, 1993).

Heavy metals discharged to the environment as industrial waste cause serious soil and water pollution. They cannot be biodegraded and thus can follow a number of different pathways. The metals can adsorb on to the soil, runoff into rivers or leach in the ground water (Mulligan, Yong, & Gibbs, 2001).

Chitosan is characterized by its ability to uptake several metal ions through different mechanisms, depending on the type of metal ion and the pH of the solution. The dissolution of chitosan is decreased through cross-linking treatments. The cross-linking procedure may be performed by reaction of chitosan with different cross-linking agents such as glutaraldehyde (Wan Ngah, Ghani, & Kamari, 2005; Monteiro Jr. & Airoidi, 1999).

The metal uptake efficiencies of chitosan and its derivatives can be enhanced via graft copolymerization of monomers of specific functional groups onto their backbones. Copper is one of the most widely used metals, which often appears in metal-bearing industrial effluents. Copper can accumulate in living microorganisms. Therefore, microbial biomass can be considered as a sorbent to remove metal ions in waste treatment plants (Ng, Cheung, & McKay, 2002).

The presence of amine groups makes a chitosan unique among biopolymers, for example, its cationic behavior in acidic solutions and its affinity for heavy metal ions (Crini, 2005; Guibal, 2005; Crini, 2006). Ion exchangers or adsorbents can be made on a large scale and low cost from chitosan. The chitosan based exchangers or adsorbents have been found potential applications in wastewater treatments to remove heavy metal ions (Crini, 2005; Dantas, Neto, Moura, Neto, & Telemaco, 2001; Boddu, Abburi, Talbott, & Smith, 2003; Li & Bai, 2005; Li, Bai, & Liu, 2005; Gavilan et al., 2009; Jin & Bai, 2002) and dyes (Chiou & Chuang, 2006; Wang & Wang, 2008).

Gyliene et al., investigated the sorption capability of chitosan for Cu^{2+} -EDTA and its regeneration by electrolysis (Gyliene, Nivinskine, & Razmute, 2006). Co^{2+} was of interest together with copper, where crab shell particles were the adsorbent (Vijayaraghavan, Palanivelu, & Velan, 2006). Fe^{2+} and Fe^{3+} sorption characteristics of chitosan and its cross-linked form were differentiated by (Ngah, Ghani, & Kamari, 2005). Chitosan modified to amine and azole resins were investigated for sorption of Hg^{2+} and UO_2^{2+} by Atia, 2005. Chitosan microspheres cross-linked with tripolyphosphate were used for the removal of both acidity and Fe^{3+} and Mn^{2+} in contaminated water from coal mines (Laus, Laranjeira, Martins, & Favere, 2006).

In our research directed towards developing new hydrogels, we chose to use chitosan because of its biodegradability and unique cationic properties. We have modified chitosan chemically with different heterocycles under different conditions (Kandile, Mohamed, Zaky, Nasr, & Abdel-Bary, 2009; Kandile & Nasr, 2009).

The objective of the research presented herein was to characterize particular chemical and physical properties of the new hydrogels prepared from reaction of chitosan with PVA and different heterocyclic compounds and to study their efficiency for metal uptake.

2. Experimental

2.1. Materials

The materials used were obtained as follows: chitosan with 67% degree of deacetylation, M.W > 6305, polyvinyl alcohol (PVA) with 88% hydrolyzed $[-CH_2CH(OH)-]_n$ powder average M.W 10,000, glutaraldehyde (G), ethanol, methanol, phthalic anhydride (Aldrich, Egypt); pyridine (El Nasr Pharmaceutical Chemicals Co., Egypt); maleic anhydride (Merck, Egypt), acetic anhydride (Alpha, Egypt), hydrazine hydrate (99%), acetic acid (glacial), dimethylsulfoxide (Fluka, Egypt), benzene (Aldrich, Egypt); dimethylformamide tetrahydrofuran (Adwic, Egypt). Copper sulfate and cobalt acetate both analytical grade were purchased from (Sigma, Egypt) and used for the preparation of the aqueous copper and cobalt solutions respectively. The following compounds were synthesized by reported methods: 1,2-bis (3-carboxyacrylyl) hydrazine (Feuer & Rubinstein, 1958), N,N'-biisomaleimide (B) (Feuer & Rubinstein, 1958), N,N'-biisophthalimide (P) (Drew & Hatt, 1937).

2.2. Measurements

Melting points were determined on a Boetius hot-stage apparatus and are uncorrected. The infrared spectra were measured on Perkin-Elmer-1430 infrared spectrophotometer using the potassium bromide Wafer technique. X-ray diffractograms of polymers were obtained with a Phillips X-ray radiation unit (Generator PW-1390) and Ni-filtered $Cu(\lambda = 1.5418 \text{ \AA})$. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out in a nitrogen atmosphere using a Shimadzo TGA-50H and DSC-50 thermal analyzer. The morphology of the different hydrogels was investigated using JXA 850 prop micro analyzer scanning electron microscope (SEM) at 600 Mm and at 1400 Mm. The solubility of the polymers was examined using 0.02 g of polymer in 3–5 ml solvents at room temperature 25 °C.

2.3. Methods

2.3.1. Synthesis of starting materials

2.3.1.1. Synthesis of 1,2-bis(3-carboxyacrylyl)hydrazine. A cold solution of hydrazine hydrate in acetic acid was prepared by slowly adding 5 g (0.1 mol) of 99% hydrazine hydrate to 25 ml of cold glacial acetic acid. This was added to a solution of 19.6 g (0.2 mol) of maleic anhydride in 100 ml of glacial acetic acid. The temperature was maintained below 25 °C throughout the addition and then the reaction mixture was let stand at 25 °C for 3 h. The crude hydrazide was filtered off, washed thoroughly with ethanol and dried in a vacuum for 3 h to yield 85% of the product, mp 185 °C (183–184 °C) (Feuer & Rubinstein, 1958).

2.3.1.2. Synthesis of N,N'-biisomaleimide. A mixture of 3 g of 1,2-bis (3-carboxyacrylyl)hydrazine in 25 ml benzene and 10 ml of acetic anhydride was refluxed for 5 h. The solid product was filtered off and crystallization from dimethylformamide gave yellow crystals of N,N'-biisomaleimide, yield: 36%, mp 260–262 °C (260 °C) (Feuer & Rubinstein, 1958).

2.3.1.3. Synthesis of N,N'-biisophthalimide. Hydrazine hydrate (2 g) in 20 ml glacial acetic acid was added during half an hour with stirring to a refluxing solution of 12 g phthalic anhydride in 40 ml of

glacial acetic acid. After 1 h, the mixture was cooled, and the precipitate removed, washed, crushed, and digested for 2 h with 400 ml of N/4-aqueous ammonia. The insoluble N,N'-biisophthalimide (5.25 g), crystallized from acetic acid to form colorless crystals, yield: 56%, mp 311–313 °C (311–313 °C) (Drew & Hatt, 1937)

2.3.2. Synthesis of the hydrogels: gelation of chitosan–PVA hydrogel

2.3.2.1. Modification of chitosan with polyvinyl alcohol. A solution of 0.56 g chitosan in 60 ml acetic acid (0.03% in distilled water) and 10 ml of polyvinyl alcohol (10% in distilled water) and 0.1 ml pyridine was refluxed with stirring for half an hour, then cooled, and evaporated. The hydrogel obtained was washed with dimethylformamide and dried under vacuum to give the corresponding hydrogel P-C-I.

2.3.2.2. Modification of chitosan with polyvinyl alcohol in presence of glutaraldehyde. A solution of 0.56 g chitosan in 60 ml acetic acid (0.03% in distilled water) and 10 ml of polyvinyl alcohol (10% in distilled water) and 5 ml of glutaraldehyde and 0.1 ml pyridine was refluxed with stirring for half an hour, then cooled and evaporated to dryness. The hydrogel obtained was washed with dimethylformamide and dried under vacuum to give the corresponding hydrogel P-C-G-(II).

3. General procedure

A mixture of heterocyclic compounds [N,N'-biisomaleimide, or N,N'-biisophthalimide] 0.5 mmol, 10 ml of polyvinyl alcohol, and 0.56 g of chitosan in pyridine was refluxed with stirring for half an hour. The hydrogel obtained after cooling was filtered, washed with dimethylformamide and dried in vacuum to give the corresponding hydrogels [P-C-B (III) and P-C-P (IV)] respectively.

3.1. Measurements of equilibrium swelling

The swelling behavior of the hydrogels was determined at 25 °C in different solvents using a cyclic swelling procedure. The swollen samples were weighed at intervals after removal of surface liquid until equilibrium swelling was attained. The swollen samples were then completely dried at 20 °C under reduced pressure and reweighed. This swelling–deswelling process was repeated three times for each sample. The percent of swelling was calculated by the following equation:

$$\text{Solvent uptake (\%)} = \frac{W_2 - W_1}{W_1} \times 100$$

where W_1 is the weight of dry hydrogel. W_2 is the weight of swollen hydrogel.

Each data point is the mean of three independent determinations.

3.2. Determination of metal ion capacity of the prepared hydrogels

Accurately weighed 50 mg of dry hydrogels samples were placed in 100 ml beakers containing 50 ml of aqueous copper sulfate or cobalt acetate solution. At regular intervals, an aliquot of supernatant solution was withdrawn. Thereafter its M^{2+} concentration was determined using UV–visible spectrometry (El-Sherbiny, 2009). The sorbed M^{2+} was calculated from the difference between the initial M^{2+} concentration and that measured at each interval. Data points are means of three independent determinations.

The efficiency of metal ion uptake of the hydrogels was calculated using the following equation:

$$F = \left(\frac{1 - C}{C_0} \right) \times 100$$

where F is the efficiency (%), C is the concentration of M^{2+} in the solution after a certain time period, C_0 is the initial concentration of M^{2+} solution.

3.3. Desorption studies

Batch processing was also used for the desorption studies. The desired amount of adsorbent for adsorption of M^{2+} was taken in a conical flask then treated for the fixed time of 8 h with 50 ml of each 0.1 M HCl, 0.1 M HNO_3 , 0.1 M NaCl, and 0.01 M EDTA solution. The amount of M^{2+} desorbed was then determined by back EDTA titration (Vogel, 1961).

4. Results and discussion

Synthesis and characterization of the new hydrogel P-C (I) and P-C-G (II).

In the present study chitosan was modified using polyvinyl alcohol in the absence or presence of glutaraldehyde to give the corresponding hydrogels [P-C (I) and P-C-G (II)] respectively.

In addition, reaction of chitosan with polyvinyl alcohol and different heterocyclic compounds such as N,N'-biisomaleimide or N,N'-biisophthalimide gave the corresponding chitosan based three component hydrogels [P-C-B (III) and P-C-P (IV)] respectively as shown in Scheme 1.

4.1. Characterization of the hydrogels

The new hydrogels were characterized by FTIR, thermal stability, morphology, crystallography, solubility, swelling capacity and metal ion adsorption.

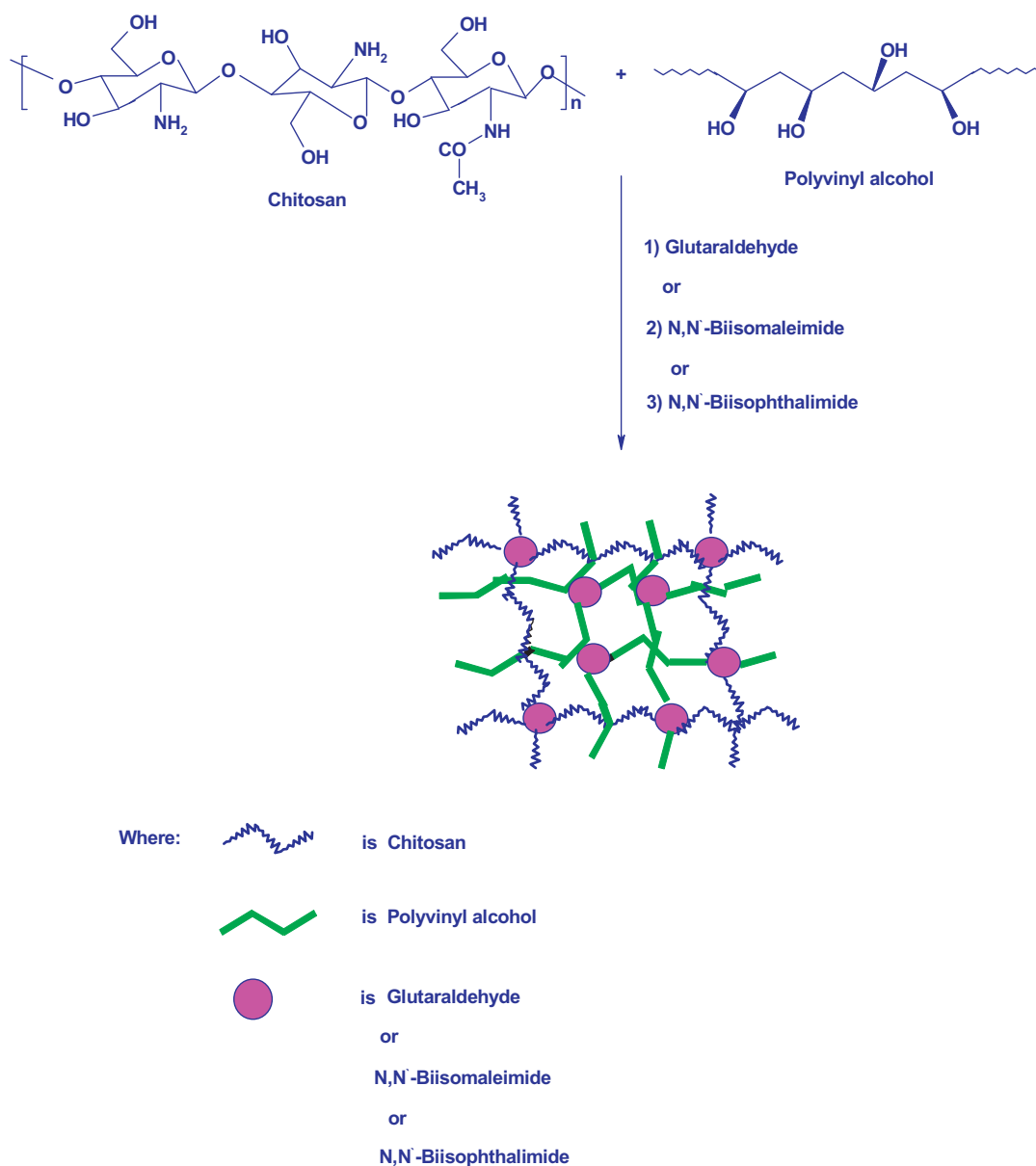
4.1.1. FTIR spectra

The FTIR spectrum for P-C(I) shows peaks at 2940 cm^{-1} due to –CH stretching, 1100 cm^{-1} due to C–OH stretching, 1654 cm^{-1} due to amide, 1412 cm^{-1} indicates the presence of carboxylic acid in the polymers, 1544 cm^{-1} peak is the symmetric deformation of $-NH_3^+$ resulting from ionization of primary amino groups in the acidic medium. Peaks at 1735 cm^{-1} are characteristic of the carboxyl C=O group. In our samples, the presence of this carbonyl group is due to the acetyl groups in chitosan.

The peak at 1260 cm^{-1} is due to the C–H vibration and that at 3450 cm^{-1} is due to OH and N–H stretching (Wang, Turhan, & Gunasekaran, 2004), whereas the FTIR spectra for (P-C-G)(II) show peaks at 1646 cm^{-1} corresponding to the formation of the imine bond C=N, due to the reaction of the amino groups of chitosan and the aldehyde groups of glutaraldehyde. The acetal and hemiacetal products of possible cross-linking reaction between the PVA and glutaraldehyde were also examined. The characteristic peaks of these hydrogels should be strongly located at 1140 cm^{-1} , 1070 cm^{-1} (Wang et al., 2004). The FTIR spectrum for P-C-B (III) shows peaks at 1074 cm^{-1} assigned to ether linkage, at 1546 cm^{-1} to the C=C stretching, at 1704 cm^{-1} to the carbonyl group of amide and at 2919 cm^{-1} for C–H aliphatic. FTIR spectra for P-C-P (IV) show peaks at 1544 cm^{-1} assigned to the C=C skeletal in-plane vibrations of the phenyl ring at 1700 cm^{-1} to the carbonyl group of amide, at 3356 cm^{-1} for (NH) and 3635 cm^{-1} for O–H as shown in Fig. 1.

4.1.2. Thermal stability

(a) Thermogravimetric analysis (TGA)



Scheme 1.

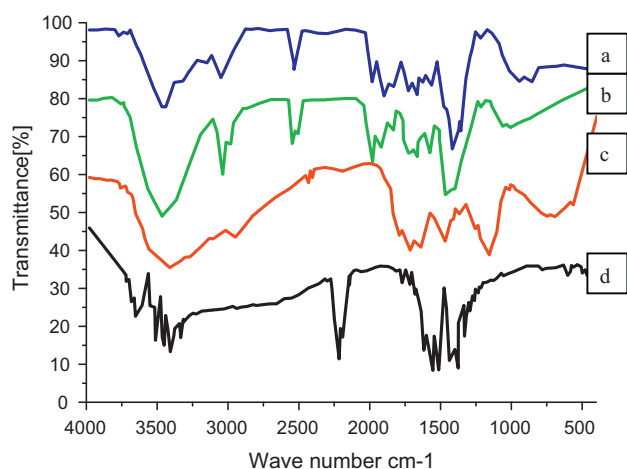


Fig. 1. FTIR spectra of the hydrogels: (a) P-C (I), (b) P-C-G (II), (c) P-C-B (III), and (d) P-C-P (IV).

The thermographs of the hydrogels were evaluated by TGA in air at a heating rate of 10 °C/min. The results of the thermogravimetric analysis of the hydrogels P-C (I), P-C-G (II), P-C-B (III), and P-C-P (IV) are given in Fig. 2 and Table 1.

The thermograph of the hydrogel P-C (I) shows that within 100 °C weight reductions can be due to moisture loss. The weight loss of the hydrogel at higher temperatures may be attributed to the decomposition of amino groups in the backbone of the polymer. However the weight loss of the crosslinked hydrogel P-C-G (II) needed higher temperatures to decompose it due to the crosslinker glutaraldehyde which improved the thermal stability of the hydrogel. The thermographs of the hydrogels [P-C-B (III) and P-C-P (IV)] show that the weight loss of the hydrogels in low temperature may be attributed to the ease of degradation of the amide groups present in the biimides, however the weight loss in the high temperature range is attributed to the degradation of the main polymer chains as shown in Fig. 2, and in Table 1.

From the above data, it is clear that the hydrogel composed of the three components polyvinyl alcohol, chitosan and N,N'-biisophthalamide [P-C-P (IV)] showed the highest thermal stability.

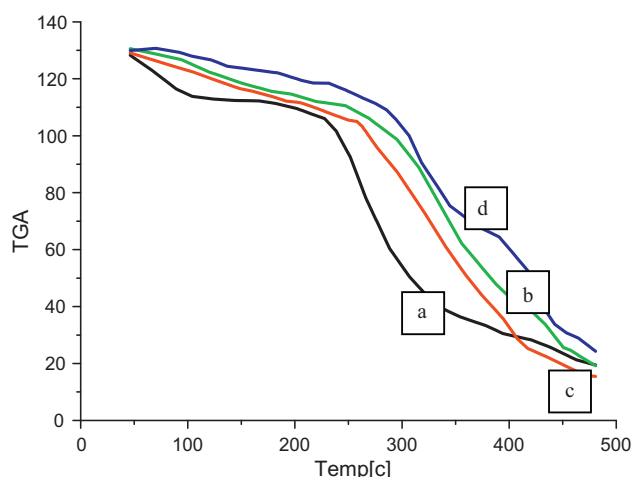


Fig. 2. TGA for: (a) P-C(I), (b) P-C-G(II), (c) P-C-B(III), and (d) P-C-P(IV).

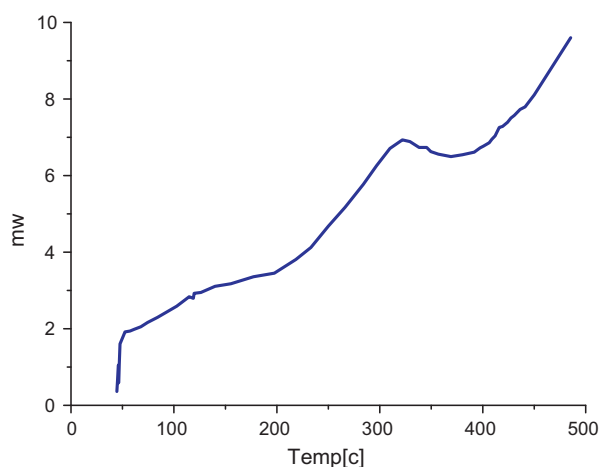


Fig. 3. DSC for: P-C-B (III).

(b) Differential scanning calorimetry (DSC):

The results of DSC analysis of the hydrogel [P-C-B (III)] are given in Fig. 3. The endothermic glass transition temperature (T_g) is at 120 °C. The high T_g value is probably related to the cross-linking, which would decrease the flexibility of the chains and the ability of the chains to undergo segmental motion, which would increase the T_g value (Saboktakin, Tabatabaee, Maharramov, & Ramazanov, 2010). Also as shown in Fig. 3 the abroad exothermic peak (T_d) at 372 °C may be attributed to the decomposition of the hydrogel indicating that the hydrogel is semicrystalline.

4.1.3. Morphology

The morphologies of the new hydrogels are revealed by SEM photographs. The SEM images of the gels are given in Figs. 4–8. Fig. 4a and b showed the surface morphology of the films for hydrogel P-C (I) at 600 μm and at 1400 μm respectively. These figures show the homogeneous surface of these films. The morphology of films of the hydrogel P-C-B (III) at 600 μm (Fig. 5a–c) indicated

Table 2

Swelling values for the hydrogels [(P-C)(I), (P-C-G)(II), (P-C-B)(III) and (P-C-P)(IV)].

| Hydrogel code | P-C | P-C-G | P-C-B | P-C-P |
|------------------|-----|-------|-------|-------|
| Solvent uptake % | I | II | III | IV |
| DMF | 171 | 100 | 182 | 193 |
| Me OH | 95 | 73 | 103 | 120 |
| DMSO | 100 | 75 | 144 | 154 |
| Water | 490 | 350 | 498 | 530 |

that the hydrogel P-C-B (III), P-C-B (III) after Cu (II) adsorption and P-C-B (III) after Co(II) adsorption respectively showed distinct differences to Fig. 4a and b and each other and confirmed the adsorption of metals by the hydrogel. Fig. 6a–c again indicated these morphological differences for the hydrogel P-C-B (III) at 1400 μm , 800 μm , 800 μm respectively. The films of the hydrogel P-C-P (IV) (Fig. 7a–c) at 600 μm indicated the hydrogel P-C-P (IV), P-C-P (IV) after Cu(II) adsorption and P-C-P (IV) after Co(II) adsorption respectively showed similar differences and confirmed the adsorption of metals in the hydrogel. Fig. 8a–c again indicate varied morphology of films of the hydrogel P-C-P (IV) at 1400 μm , 800 μm , 800 μm respectively. The homogeneous surfaces of most of these films indicate that the hydrogels are pure without residue in the product. They differ considerably from the film [(P-C)(I)] produced from reaction of chitosan with polyvinyl alcohol which confirmed that the reaction has occurred.

4.1.4. X-ray diffraction

The X-ray diffraction patterns of the hydrogels [P-C(I), P-C-G(II), P-C-B(III), and P-C-P(IV)] show that crystallinity is present in the new hydrogels. The X-ray diffraction patterns of the three components hydrogels also indicate greater amorphous properties than that of modified chitosan in absence and presence of glutaraldehyde hydrogels [P-C(I), P-C-G(II)]. This is due to the increasing degree of crosslinking in the hydrogels as shown in Fig. 9. The interfering peaks at 2θ in the range 4–90° indicate the intermediate properties of hydrogels between crystalline and amorphous leading to amorphous properties.

The X-ray diffraction pattern of the hydrogel [(P-C)(I)] shows higher crystallinity than the three component hydrogels and the lowest crystallinity is seen for the hydrogels produced from the reaction of polyvinyl alcohol with chitosan and N,N'-biisomaleimide (P-C-B)(III) however the highest crystallinity seen is for hydrogels produced from the reaction of polyvinyl alcohol with chitosan and N,N'-bisophthalimide (P-C-P)(IV).

4.1.5. Solubility

The solubility test for the new hydrogels [(P-C)(I), (P-C-G)(II), (P-C-B)(III) and (P-C-P)(IV)] was studied in different solvents at room temperature. The hydrogels were found to be insoluble in different organic solvents such as DMF, DMSO, THF, NMP, chloroform, acetone, and methanol.

4.1.6. Swelling measurements

The swelling values of the hydrogels (P-C)(I), (P-C-G)(II), (P-C-B)(III) and (P-C-P)(IV) were obtained from heating the hydrogels in a solvent at its boiling point and are shown in Table 2.

The presence of the hydrophilic amino and amide groups is known to increase the hydrophilicity of the system and con-

Table 1

Thermal properties of the hydrogels [(P-C)(I), (P-C-G)(II), (P-C-B)(III) and (P-C-P)(IV)].

| Hydrogel code | Temp | Wt. loss (%) | Temp | Wt. loss (%) | Temp | Wt. loss (%) | Temp | Wt. loss (%) |
|---------------|------|--------------|------|--------------|------|--------------|------|--------------|
| (P-C)(I) | 80 | 2.8 | 120 | 5.9 | 380 | 44.7 | 500 | 7.5 |
| (P-C-G)(II) | 180 | 12.1 | 340 | 28.7 | 470 | 36.2 | 500 | 2.6 |
| (P-C-B)(III) | 110 | 8.2 | 375 | 49.6 | - | - | - | - |
| (P-C-P)(IV) | 100 | 6.7 | 195 | 9 | 350 | 42.5 | 450 | 18.7 |

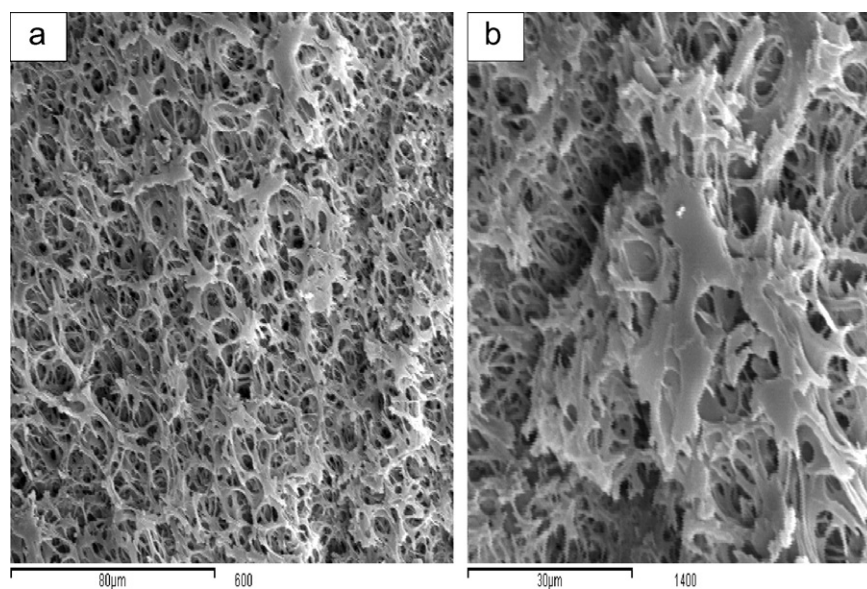


Fig. 4. (a) SEM of P-C (I) at 600 Mm. (b) SEM of P-C (I) at 1400 Mm.

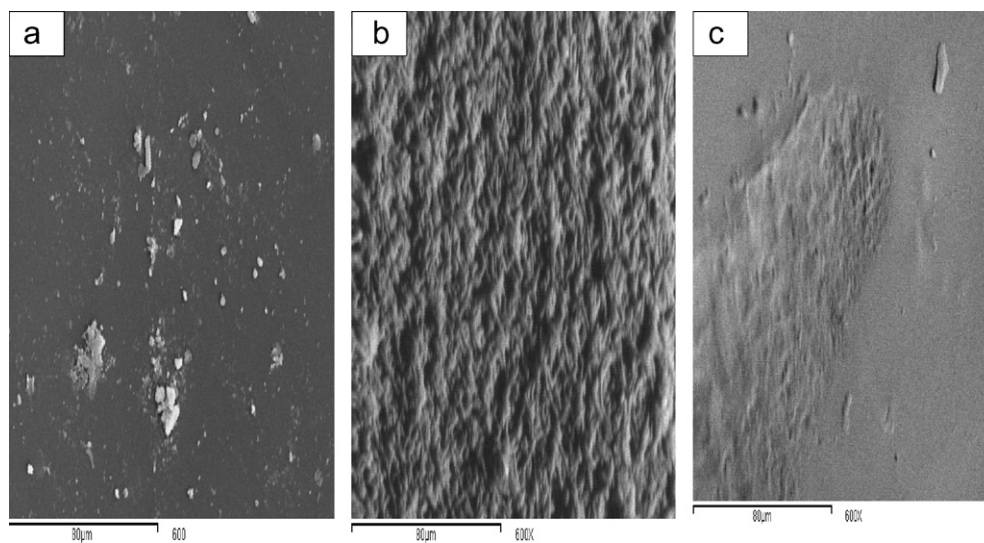


Fig. 5. (a) SEM of P-C-B (III) at 600 Mm. (b) SEM of P-C-B (III) after Cu(II) adsorption at 600 Mm. (c) SEM of P-C-B (III) after Co(II) adsorption at 600 Mm.

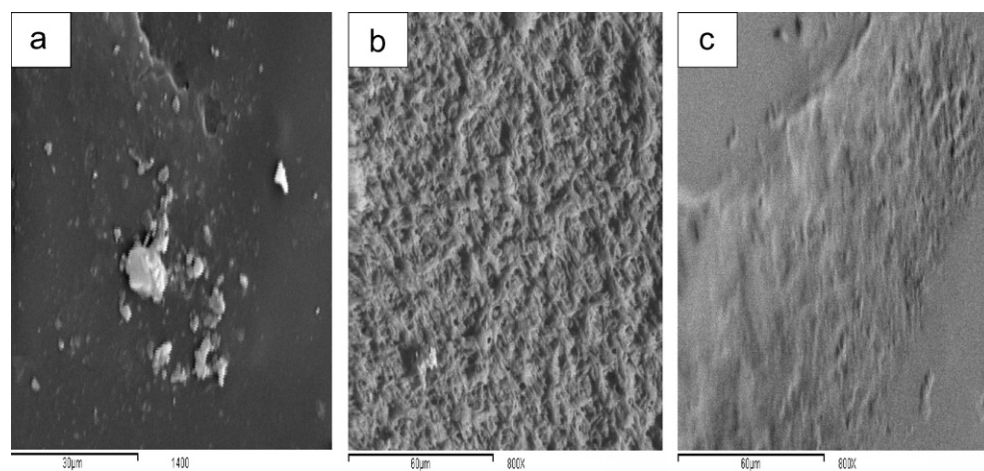


Fig. 6. (a) SEM of P-C-B (III) at 1400 Mm. (b) SEM of P-C-B (III) after Cu(II) adsorption at 800 Mm. (c) SEM of P-C-B (III) after Co(II) adsorption at 800.

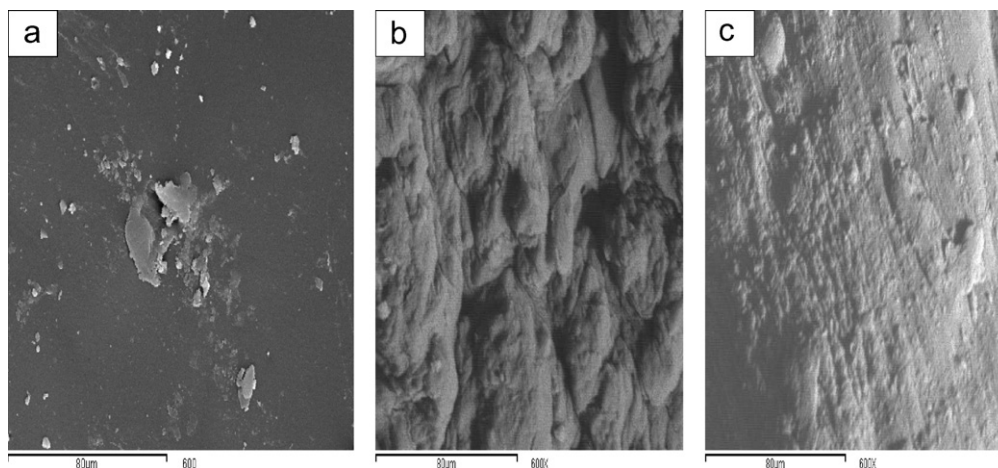


Fig. 7. (a) SEM of P-C-P (IV) at 600 Mm. (b) SEM of P-C-P (IV) after Cu(II) adsorption at 600 Mm. (c) SEM of P-C-P (IV) after Co(II) adsorption at 600 Mm.

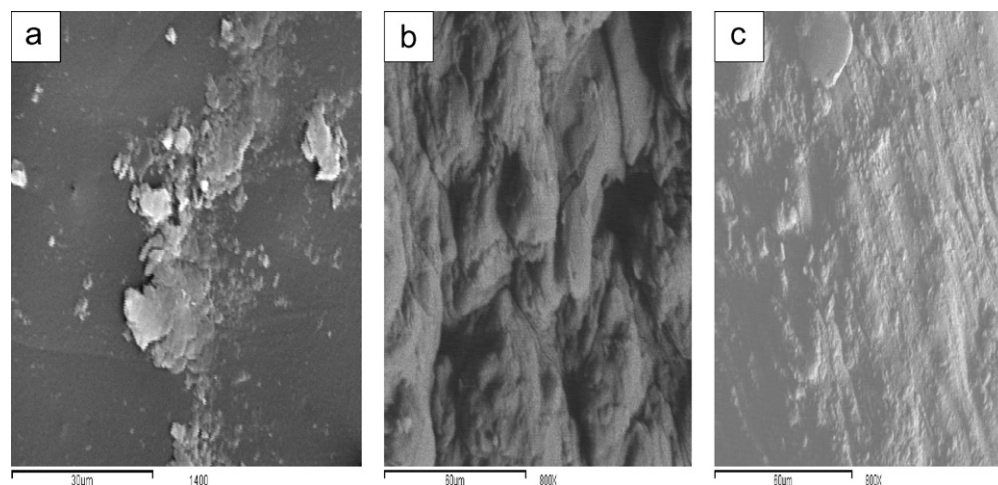


Fig. 8. (a) SEM of P-C-P (IV) at 1400 Mm. (b) SEM of P-C-P (IV) after Cu(II) adsorption at 800 Mm. (c) SEM of P-C-P (IV) after Co(II) adsorption at 800 Mm.

sequently they increase the equilibrium swelling values of the samples in aqueous medium.

From Table 2, the highest degree of swelling capacity for the hydrogels is observed with water as opposed to the aprotic solvents. It is readily noted that the hydrogel (P-C-P)(IV) possessed highest degree of swelling capacity in the solvents studied and the hydrogel (P-C-B)(III) possessed a lower degree of swelling capacity than the others. This indicates that the hydrogel produced from reaction of polyvinyl alcohol and chitosan with N, N'-biisomaleimide (P-C-B)(III) contained the higher degree of crosslinking of the two.

4.1.7. Metal ion entrapment

A preliminary study was carried out to evaluate the copper and cobalt metal ion uptake capacity of the new hydrogels from aqueous systems. The metal ion uptake increases with increasing time of immersion of the hydrogels as shown in Tables 3 and 4. This may be attributed to the increase of the number of chelating side chains of the hydrogels to form complexes with M^{2+} ions.

The data in Tables 3 and 4 indicated that the highest efficiency of the hydrogels for Cu^{2+} and Co^{2+} ion uptake was obtained from the hydrogel resulting from reacting chitosan with polyvinyl alcohol

and N,N'-biisophthalimide [(P-C-P)(IV)] (52.5%) and (72.5%) respectively.

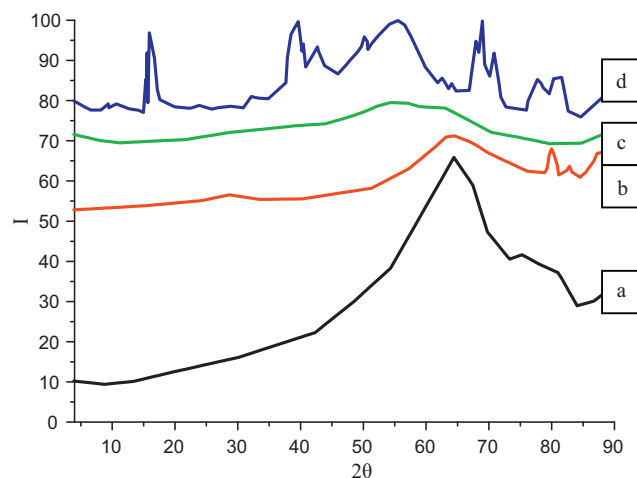


Fig. 9. X-ray diffraction pattern of: (a) P-C (I), (b) P-C-G (II), (c) P-C-B (III), and (d) P-C-P (IV).

Table 3Effect of immersion time of different hydrogels and their efficiency for Cu²⁺ uptake.

| Hydrogel | Immersion time (h) | Cu ²⁺ (g/l) | Efficiency (%) |
|------------|--------------------|------------------------|----------------|
| P-C(I) | 0 | 2.0 | – |
| | 5 | 1.65 | 17.5 |
| | 10 | 1.36 | 32 |
| P-C-G(II) | 0 | 2.0 | – |
| | 5 | 1.9 | 5 |
| | 10 | 1.85 | 7.5 |
| P-C-B(III) | 0 | 2.0 | – |
| | 5 | 1.63 | 18.5 |
| | 10 | 1.27 | 36.5 |
| P-C-P(IV) | 0 | 2.0 | – |
| | 5 | 1.3 | 35 |
| | 10 | 0.95 | 52.5 |

Table 4Effect of immersion time of different hydrogels and their efficiency for Co²⁺ uptake.

| Hydrogel | Immersion time (h) | Co ²⁺ (g/l) | Efficiency (%) |
|------------|--------------------|------------------------|----------------|
| P-C(I) | 0 | 2.0 | – |
| | 5 | 1.36 | 32 |
| | 10 | 1.2 | 40 |
| P-C-G(II) | 0 | 2.0 | – |
| | 5 | 1.41 | 29.5 |
| | 10 | 1.32 | 34 |
| P-C-B(III) | 0 | 2.0 | – |
| | 5 | 1.26 | 37 |
| | 10 | 1.0 | 50 |
| P-C-P(IV) | 0 | 2.0 | – |
| | 5 | 1.2 | 40 |
| | 10 | 0.55 | 72.5 |

Thus results showed that these hydrogels may be used as effective materials for metal ion removal from aqueous systems.

5. Conclusions

New crosslinked hydrogels based on chitosan have been synthesized and characterized. Chitosan based hydrogels were prepared through modification of chitosan with polyvinyl alcohol in the absence or presence of glutaraldehyde and heterocyclic compounds such as N,N'-biisomaleimide and N,N'-biisophthalimide under different reaction conditions. The swelling behavior of the hydrogels was dependent on the heterocyclic moieties and produced increased swelling of hydrogels in different organic solvents. The N,N'-biisophthalimide hydrogel showed the highest swelling values in different organic solvents.

The adsorption capacity of all the new hydrogels for metal ions Cu²⁺ and Co²⁺ ions, from aqueous systems showed various levels of efficiency. Thus the new hydrogels may be used for treatment of industrial waste water and other waters polluted with heavy metals.

The metal ion uptake data for the hydrogel produced from chitosan–polyvinyl alcohol–N,N'-biisophthalimide [(P-C-P)(IV)] showed the highest adsorption capacity for Cu²⁺ ions with efficiencies reaching 52.5%, and for Co²⁺ ions 72.5% respectively.

From the thermal stability studies of these new hydrogels, chitosan–polyvinyl alcohol–N,N'-biisophthalimide [(P-C-P)(IV)] was shown to be of higher stability than that the hydrogel chitosan–polyvinyl alcohol–N,N'-biisomaleimide [(P-C-B)(III)]. It was also clear that modification of chitosan with polyvinyl alcohol in presence of glutaraldehyde improved thermal stability.

From the above data it can be concluded that the introduction of the heterocyclic moiety N,N'-biisophthalimide to chitosan produced the better hydrogel.

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