American Journal of Chemistry and Materials Science
2014; 1(4): 24-29
Published online January 30, 2015 (http://www.openscienceonline.com/journal/ajcms)

Substantial performance of silane surface treated 1, 4 butane diol /hydroxyapatite biocomposite hydrogels for dye removal applications

Franklin D. S.[1], Guhanathan S.[2, *]

[1]Department of Chemistry, C. Abdul Hakeem College of Engineering and Technology, Melvisharam, Tamilnadu, India
[2]PG & Research Department of Chemistry, Muthurangam Government Arts College (Autonomous), Vellore, Tamilnadu, India

Email address

loyolafrank@yahoo.co.in(Franklin D. S.), sai_gugan@yahoo.com (Guhanathan S.)

To cite this article

Franklin D. S., Guhanathan S.. Substantial Performance of Silane Surface Treated 1, 4 Butane Diol /Hydroxyapatite Biocomposite Hydrogels for Dye Removal Applications. *American Journal of Chemistry and Materials Science*. Vol. 1, No. 4, 2014, pp. 24-29.

Abstract

pH-sensitive biocomposite hydrogels (ACBD-HA) have been synthesized using butane diol (BD), citric acid (CA), acrylic acid (AA) and hydroxyapatite (HA) in the absence of organic solvents. HA was surface treated with two different silane based coupling agents viz., 3-aminopropyltrimethoxysilane (AMS) and vinyltriethoxysilane (VES). The results of the studies reveal that VES surface treated hydroxyapatite biocomposite hydrogels found to have superior properties (swelling, thermal and removal of methylene blue) than AMS and untreated ACBD-HA. This kind of hydrogels might have greater potential in many areas, such as hygiene products, pharmacological, agricultural and eco-friendly applications.

Keywords

Thermal Analysis, Swelling Equilibrium, Cationic Dye, Composite Hydrogels

1. Introduction

Organic –inorganic hybrid biocomposite material based on natural polymer and inorganic components received considerable responsiveness due to excellent properties superior to each individual component as well as an environment friendly characteristic. However, mild devotion have been paid on the application of HA as an inorganic additive of composite hydrogels [1-2]. Synthetic dyes are broadly used in many fields such as textile, leather, paper, rubber, plastics, cosmetics, pharmaceutical, and food industries [3]. Synthetic dyes usually have a complex aromatic molecular structure and exhibit considerable structural diversity. Dye damaging the environment, which must remove from water before discharged in to environment. It is difficult to treat polluted water using conventional methods [4]. Anionic and cationic hydrogels have used as an adsorbent to treatment of waste water containing dye pollutants [5-6]. Hydrogels are three-dimensional polymeric network with segments of hydrophilic groups. It is an interesting material from the perspective of basic sciences as well as potential applications in various fields like engineering and medical. The polymeric structures are elastic and change their volume in contact with aqueous solutions by holding a large amount of water while maintaining the structure [7]. pH sensitive polymeric hydrogels that undergo controllable volume changes in response to small variation in pH. Swelling is an important character to decide the applications of hydrogels. The nature of swelling can be tailored by a rational and proper selection of hydrogel building blocks. Citric acid (CA) is a multi-functional, renewable, nutritionally harmless, nontoxic, readily available and cost effective monomer [8]. Butane diol (BD) was chosen as a difunctional monomer to improve the properties of hydrogels because of its flexibility and biocompatibility. Acrylic acid is a monomer to fabricate pH–sensitive hydrogels [9]. Eggshells are one of the richest sources of calcium, which can be utilized for the synthesis of hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) [10]. It is an ideal material for its excellent properties like biocompatibility, non-toxic, low-cost. HA with hydrophilic biopolymeric matrix, expected to have enhanced properties of inorganic and organic components.Silane coupling agents (AMS and VES) used to

generate organic layer over HA and improve adhesion (or) interfacial bonding between the HA and the polymer matrix [11]. The highlights of the present investigation have shown (i) No organic cross-linker was used (ii) Synthesis of biocomposite hydrogels were programmed by renewable resource based constituents (iii) No organic solvent used thoroughly in the investigation (iv) Hydroxyapatite prepared from waste eggshells (v) Surface modification was performed with silane coupling agents (vi) The improved performances in swelling, thermal and removal dye were also observed.

The primary objective of this study was to synthesize a butane diol based biocomposite hydrogels with tuned pH-sensitivity using solvent-free green approach. The structural characterization, thermal studies and morphologies of biocomposite hydrogels were studied by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction studies (XRD), thermal studies (TGA, DTG) and the scanning electron microscope (SEM). Furthermore, the effect of silane based coupling agents on thermal and morphological aspects of biocomposite hydrogels has also been investigated. The synthesized new kind of materials with improved network structure and performance properties have also been examined comprehensively.

2. Experimental

2.1. Materials

The monomer anhydrous citric acid (CA), acrylic acid (AA), aminopropyltrimethoxysilane (AMS) and vinyltriethoxysilane (VES) were obtained from Sigma-Aldrich. Prior to use, AA was vacuum distilled at 54°C/ 25 mm Hg to remove the inhibitor hydroquinone. Butane diol (BD) and methanol were purchased from Merck (India). Eggshells were collected domestically. Demineralized water was used for the preparation of the buffer solutions.

2.2. Synthesis of ACBD-HA, ACBD-HA-AMS and ACBD-HA-VES Biocomposite Hydrogels

The synthesis of the hydroxyapatite from waste eggshells and their surface modification by silane coupling agents namely, 3-aminotrimethoxy silane and vinyl triethoxysilane was the same as published recently by our research group [7]. Surface modified silane hydroxyapatite was denoted as HA-AMS, HA-VES respectively. The hydrogels (ACBD) was synthesized according to our previous contribution [8-9]. The citric acid (0.025 mol) was mixed with 1, 4 butane diol (0.025 mol) in the presence of an acidic medium for 1 h at 140 °C resulting in a white colored sticky gel-like compound (CBD). Acrylic acid (0.025 mol) was added to pre-polyester CBD at 140 °C with constant stirring for 2 h in the nitrogen atmosphere. The formation of glassy gel (ACBD) was considered as completion of the reaction. Subsequently, 0.2 g of HA and surface treated HA were added to a separate reaction vessel which contains biopolymeric hydrogel (ACBD) resulted biocomposite hydrogels ACBD-HA, ACBD-HA-AMS and ACBD-HA-VES respectively.

2.3. Characterization and Measurements

The structural information of biocomposite hydrogels were accomplished by using FTIR (FTIR-8400 S, Shimadzu spectrophotometer). SEM was performed on dried biocomposite hydrogel samples using Hitachi, Model: S-3400. Thermal properties of composite hydrogel was determined by thermo gravimetric analysis (TGA) and DTG (Perkin Elmer-Diamond) in the temperature ranging from ambient to 500 °C at the heating rate of 10 °C min^{-1}, under N_2 atmosphere. The swelling equilibrium of dried biocomposite hydrogels were immersed in the swelling medium (pH= 4.0–10.0).The XRD apparatus (Philips PW 1820) powder diffractometer was used to investigate the crystallinity and phase content of biocomposite hydrogels. Using Scherrer's formula size of HA particle was calculated [14].

$$D = \frac{0.89\lambda}{\beta \cos\theta} \tag{1}$$

The synthetic aqueous solutions of methylene blue (MB) dye were prepared in the concentration ranges 25-250 ppm. Dry 0.1 g of hydrogel was transferred into 100 mL of the MB dye solution (250 ppm) and allowed to equilibrate for 24 h at room temperature. These solutions were separated superficially by decantation from the hydrogels. Spectrophotometric measurements were carried out using a Shimadzu 160A model Ultraviolet-Visible spectrophotometer at ambient temperature. Distilled water was chosen as the reference. The equilibrium concentrations of dye solutions were found by means of pre calibrated scales. Spectrophotometric methods were utilized to follow the concentrations of these dye solutions.

$$R(\%) = \frac{C_0 - C_e}{C_0} \times 100 \tag{2}$$

$$q_e = \frac{C_0 - C_e}{W} \times V \tag{3}$$

The percentage of MB removal percentage (R) is calculated according to Eq. (3) Where, C_0 (mg/L) and C_e (mg/L) are the initial and the equilibrium concentrations of MB, respectively, V (L) is the solution volume and W (g) is the composite mass [15].

3. Results and Discussion

3.1. FT-IR Spectral Studies of Biocomposite Hydrogels

The FT-IR spectra of ACBD-HA biocomposite hydrogel has been shown in Figure 1a, from which intensification of the bands at wave numbers 591.44, 935.20 and 1033.17 cm^{-1} could be attributed to PO_4^{3-} indicated a successful inclusion of HA in ACBD. Incorporation of AMS modified HA in the

ACBD, new absorption bands were observed at 1391.13 and 793.08, 897.16, 980.37 cm^{-1} which has been attributed to Si-O stretching and bending vibration respectively. The overlay FT-IR spectra of ACBD-HA-VES composite hydrogel was presented in Figure 1c, which revealed that new bands were also observed at 939.31, 796.67 cm^{-1} which could be related to Si-O stretching and bending vibration. A weak shoulder peak has been noticed 2939.04 cm^{-1}, which correspond to the aliphatic CH stretching of polymer backbone and Si $(CH_2)_3$ stretching frequencies [13]. In general, all the biocomposite hydrogels have shown broad hydrogen bonded OH (~3200-3600 cm^{-1}), ester carbonyl, C-O and COO- stretching confirmed the structure of composite hydrogels.

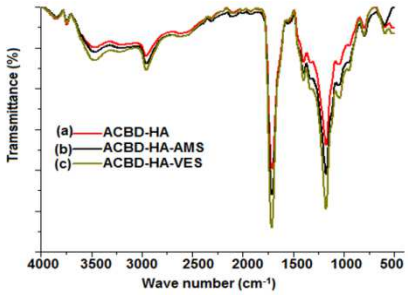

Fig. 1. *Comparative FT-IR spectra of (a) ACBD-HA (b) ACBD-HA-AMS (c) ACBD-HA-VES.*

3.2. XRD Studies of Biocomposite Hydrogels

The XRD pattern of HA and ACBD-HA biocomposite hydrogel were shown in Figure 2. The peaks of synthesized HA particle matched the XRD pattern of HA (JCPDS No: 09-0432). As seen from Figure 2a, ACBD-HA, the peaks observed at 30, 33 and 41 ° (2θ region) were characteristic peaks of HA [16].

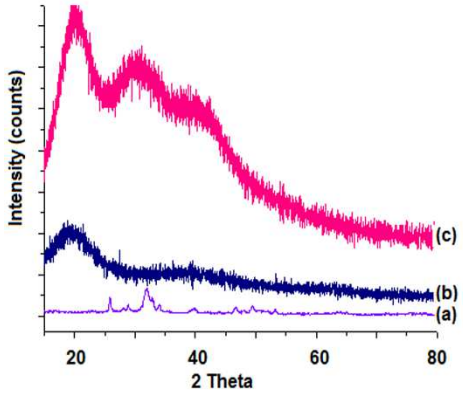

Fig. 2. *Comparative X-ray diffraction pattern for (a) HA (b) ACBD (c) ACBD –HA*

The absence of additional peaks has indicated that the biocomposite hydrogel was highly amorphous. The XRD pattern of biocomposites is slightly broader than that of pure HA which might be due to the interaction of polymer matrix with hydroxyapatite. Further, the mean crystallite has calculated by Scherrer's equation of the composite approximately (28-30 nm) less than 50nm [17].

3.3. Morphologies of Biocomposite Hydrogels

The surface morphology of the hydrogel (ACBD) showed smooth and perfect homogeneity among the ingredients.

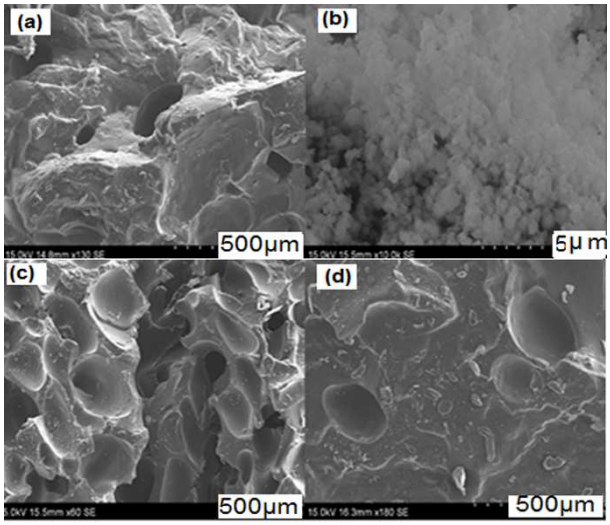

Fig. 3. *Scanning electron microscope picture of (a) HA (b) ACBD (c) ACBD-HA-AMS (d) ACBD -HA-VES.*

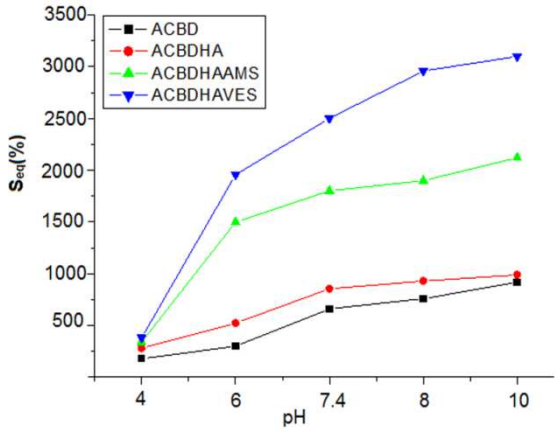

Fig. 4. *Swelling equilibrium of biocomposite hydrogels ACBD, ACBD-HA, ACBD-HA-AMS, ACBD -HA-VES at various pH from 4.0-10.0*

SEM images of ACBD-HA (Figure 3b) biocomposite hydrogel revealed that the presence of HA particles were sprinkled inside the polymer matrix. Incorporation of HA into the ACBD (Figure 3a) modifies the original polymer structure by increasing the swelling of biocomposite hydrogel. As could be seen in the Figure 3c, ACBD-HA-AMS obtained have exhibited mostly connected circular and elliptical pores. ACBD-HA-VES biocomposite hydrogel (Figure 3d) with uneven dispersed HA particle were present, which tunes the irregular large pores and channels within the polymer matrix. Furthermore, it encouraged the fluid to easily enter into the gaps, leading to a substantial increase of the absorption than that of ACBD-HA and ACBD-HA-AMS biocomposite hydrogels. Furthermore, the presence of negatively charged ions in HA facilitating the osmotic swelling pressure originated from the counter ion within the biopolymeric hydrogels.

3.4. Equilibrium Swelling Studies of Biocomposite Hydrogels

The S_{eq}% (Figure 4) value of ACBD-HA hydrogel was found to have 280.00, 523.00, 854.00, 928.70 and 989.90 % at pH 4.0, 6.0, 7.4, 8.0 and 10.0 respectively. Similarly, ACBD-HA-AMS and ACBD-HA-VES were listed as 340.00, 1500.00, 1800.00, 1900.00, 2120.00% and 383.00, 1958.00, 2500.00, 2960.00 and 3100.00% at pH 4.0, 6.0, 7.4, 8.0 and 10.0 respectively. The S_{eq}% of composite hydrogels were significantly higher at higher pH, compared to the lower pH value.

3.4.1. Thermal Characterization of Biocomposite Hydrogels

10% weight loss of ACBD-HA, ACBD-HA-AMS and ACBD-HA were observed at 163, 220 and 225 °C have shown in Figure5. This clearly implied that the introduction of HA into the polymer matrix enhances the thermal stability. It could be seen from Figure 5a, ACBD-HA biocomposite hydrogel has three stages of degradation. The first stage ranges between 90-162 °C corresponding to 7 % loss in weight might be due to the loss of absorbed water. The second stage of weight loss has started at 210 °C and progressed up to 352 °C with weight loss 28.00%. The third stage degradation have observed at 268-352 °C with weight loss about 29% might be related to the cleavage of another composition of composite hydrogel and carbonization of the polymeric materials.

TGA curves of ACBD-HA-AMS composite hydrogels have shown in Figure 5b. In general, the weight loss have been listed in three stages: the first stage was the loss of structural water of the hydrogels ambient to 175 °C with weight loss of 40.00%. The second stage of decomposition occurs at (240-309 °C), with 25.00% weight loss due to the thermal degradation of the polymeric chains was due to the carbonization of the polymeric materials. The thermograph of the ACBD-HA-VES (Figure 5c) showed that the first stage of decomposition has been observed from 100-198 °C with 8% weight loss, might be due to moisture. Second stage decomposition has started at 245 °C and proceeded up to 297 °C with 26% weight loss. Third stage decomposition identified at 297 °C and continued up to 460 °C with 27.00% weight loss. TGA thermograms were well supported by DTG curves. The improved thermal stability was observed. In general, for silane surface modified hydroxyapatite than untreated one.

3.5. Dye Removal Studies of Biocomposite Hydrogels

The influence of pH on hydrogels of cationic dye in to hydrogels was investigated and they were presented in Figure 6. The adsorption capabilities of biocomposite hydrogels and surface treated composite hydrogels for removal (R %) of methylene blue from aqueous solutions were examined. The series of four different glycerol based hydrogels (ACBD-HA, ACBD-HA-AMS and ACBD-HA-VES) biocomposite hydrogels have shown (R %) for all sample exhibited maxima at a higher pH than lower pH.

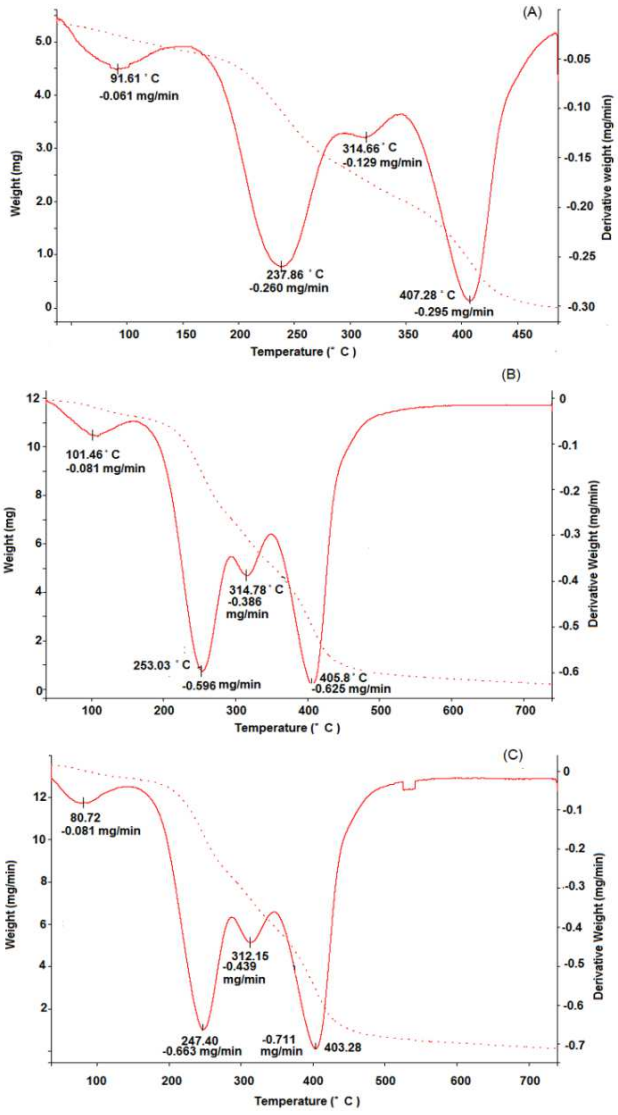

Fig. 5. TGA-DTG Curve of (a) ACBD-HA (b) ACBD-HA-AMS (c) ACBD-HA-VES

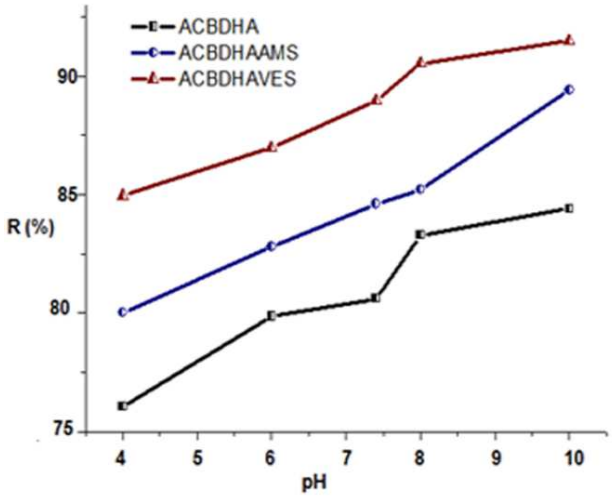

Fig. 6. pH sensitivedye removal studies of biocomposite hydrogels ACBD-HA , ACBD-HA-AMS, ACBD-HA-VES.

The RE (%) value of ACBD-HA hydrogel at pH 4.0, 6.0, 7.4, 8.0 and 10.0 were 76.06, 79.86, 80.62, 83.28 and 84.40% respectively by comparing these values with ACBD-HA-AMS, (R%) values were found to have 80.0, 82.80, 84.60, 85.20 and 89.40% and for ACBD-HA-VES treated biocomposite hydrogel recorded highest removal efficiency of 84.95, 86.98, 88.96, 90.54 and 91.48% at pH 4.0, 6.0, 7.4, 8.0 and 10.0 respectively. In overall observation VES surface modified biocomposite hydrogels have shown an excellent dye removal capacity. The amount of MB adsorbed was measured spectrophotometrically in periodically taken solution samples. VES treated composite hydrogels have exhibited excellent maximum dye removal tendency than AMS treated and untreated hydrogels. The results indicated that, dye uptake of hydrogel increases with increasing pH from 4.0-10.0. [18].

Table 1. *Adsorption equilibrium of various biocomposite hydrogels (pH 4.0-10.0)*

pH	ACBD-HA	ACBD-HA-AMS	ACBD-HA-VES
4	190.15	200.00	212.375
6	199.65	207.00	217.45
7.4	201.55	211.50	222.40
8.0	208.20	213.00	226.35
10	211.00	223.50	228.70

The adsorption capacity (q_e) of the series of hydrogels on methylene blue was presented in Table 1. The adsorption experiments were executed at 250 ppm of (MB) with respect to different pH (4.0-10.0). It has been clearly designated from the table that q_e was significantly higher at higher pH, when compared to lower and neutral pH. The maxima q_e value observed at VES surface treated hydrogels. Adsorption efficiency experiment was conducted for 24 hours. Biocomposite hydrogels were reached equilibrium for 24h. There are two main reaction dominated in the mechanism of adsorption of cationic dye onto hydrogels, (i) Electrostatic interaction between dyes and adsorbent (ii) Possible chemical reaction of N^+ groups of the dyes and COO^- groups of the hydrogels [19].

4. Conclusions

pH-sensitive biocomposite hydrogels of citric acid were synthesized utilizing butane diol, acrylic acid and hydroxyapatite. The spectral techniques such as FT-IR and XRD analysis supported the formation of biocomposite hydrogels. The enhanced performances in swelling and thermal stability have been noticed for silane treated composite hydrogels. Thermal stability of the hydrogels has been investigated by TGA-DTG. In ACBD-HA-VES biocomposite hydrogel, HA particle were unevenly dispersed and tunes the swelling, it encouraged the fluid to easily enter into the gaps, than that of ACBD-HA and ACBD-HA-AMS. The improved thermal stability was observed for silane surface modified hydroxyapatite than untreated one. Surface treated biocomposite hydrogels have shown an excellent dye removal and adsorption efficiency, the ascending order as follows ACBD-HA<ACBD-HA-AMS<ACBD-HA-VES. The synthesized biocomposite hydrogels could be utilized for the pharmaceuticals, agricultural and environmental applications.

References

[1] Darder M, Colilla M., Ruiz-Hitzky E. Biopolymer-clay nanocomposites based on chitosan intercalated in montmorillonite, Chem Mater2003; 15:3774-3780.

[2] Delhom CD, White LA, Pang SS. Development and characterization of cellulose/clay nanocomposites, Composites Part B 2010; 41: 475-481.

[3] Jain R, Gupta VK, Sikarwar S. Adsorption and desorption studies on hazardous dye Naphthol Yellow S, J Hazard Mater 2010; 182: 749–756.

[4] Bajpai SK, Shrivastava S. Sorptive removal of methylene blue from aqueous solutions by polymer/activated charcoal composites, JAppl PolymSci 2011; 119: 2525–2532.

[5] Li S, Liu X, Zou, T, Xiao W.Removal of cationic dye from aqueous solution by a macroporous hydrophobically modified Poly(acrylic Acid-acrylamide) hydrogel with enhanced swelling and adsorption properties. CLEAN – Soil, Air, Water 2010; 38:378–386.

[6] SolpanD, DuranS, Torun,M. Removal of cationic dyes by poly(acrylamide-co-acrylic acid) hydrogels in aqueous solutions. Rad Phy Chem2008; 77: 447–452.

[7] Ichikawa H. Hydrogels in Pharmaceutical Formulations. Eur J Pharm Biopharm 2000; 50: 27-46.

[8] Yang J, Motlagh D, Allen JB, Webb AR, Kibbe MR, Aalami, O , Kapadia M, Carroll TJ, Ameer G.A. Modulating expanded polytetrafluoroethylene vascular graft host response via citric acid-based biodegradable elastomers, Adv. Mater 2006; 18: 1493-1498.

[9] ZhouY,FuS, ZhangL, ZhaH. Superabsorbent nanocomposite hydrogels made of carboxylated cellulose nanofibrils and CMC-g-p(AA-co-AM).Carbohydr Polym 2013; 9: 429–435.

[10] Rivera EM, Araiza M, Brostow W, Castano VM, Diaz-Estrada J R. Hernandez, R. , Rodriguez, J.R. Synthesis of hydroxyapatite from eggshells. Mater Lett 1999; 41:128-134.

[11] Franklin DS, GuhanathanS.Performance of silane coupling agent treated hydroxyapatite /diethylene glycol based pH-sensitive biocomposite hydrogels. Iran Polym J2014;*23:* 809-817.

[12] Franklin DS, Guhanathan,S. Synthesis and characterization of citric acid based pH sensitive biopolymeric hydrogels. Polym Bull 2014; 71: 93-110.

[13] Franklin D.S, Guhanathan,S. Influence of chain length of diol on the swelling behavior of citric acid based pH sensitive polymeric hydrogels - A Green approach. JAppl PolymSci 2015; 132: 41403.

[14] Wang X, Maa J, Wang Y,He B. Bone repair in radii and tibias of rabbits with phosphorylated chitosan reinforced calcium phosphate cements. Biomaterials 2002; 23: 4167–4176.

[15] Wang, Y, Zeng L,Ren X, Song H. Removal of Methyl Violet from aqueous solutions using poly (acrylic acid-co-acrylamide)/attapulgite composite. J Environ Sci 2010; 22, 7-14.

[16] Kalambettu AB, Rajangam P, Dharmalingam, S.The effect of chlorotrimethylsilane on bonding of nano hydroxyapatite with a chitosan-polyacrylamide matrix.Carbohydr Res 2012; 352: 143-150.

[17] Nikpour, M.R., Rabiee, S.M., Jahanshahi, M. Synthesis and characterization of hydroxyapatite/chitosan nanocomposite materialsfor medical engineering applications. Composites Part B*:* Engineering 2012; 43:1881-1886.

[18] Solpan D, Kolge Z. Adsorption of methyl violet in aqueous solutions by poly(N-vinylpyrrolidone-co-methacrylicacid) hydrogels. Rad Phy Chem 2006;75, 120-128.

[19] ErenZ, AcarFN Adsorption of Reactive Black 5 from an aqueous solution: equilibrium and kinetic studies, Desalination 2006;194:1–10.