

Synthesis and Characterization of Cellulose-based Eco-Friendly Hydrogels

Md. Obaidul Haque and Md. Ibrahim H. Mondal*

Polymer and Textile Research Lab, Department of Applied Chemistry and Chemical Engineering, University of Rajshahi, Rajshahi 6205, Bangladesh.

*Corresponding author: *mihmondal@yahoo.com*

Abstract

Biodegradable nature of hydrogels is highly appreciable and core expectation at present time. Cellulose and cellulose derivatives can be copolymerized in producing green hydrogels for improving the absorption performance of many adsorbent products. Hydrogels are polymeric substances and due to hydrophilic functional groups in their structure capable of holding large amount of water compared to its body mass. Crosslinking is one of the simplest reactions used to improve the physico-chemical properties of cellulose and cellulose derivatives. In the present paper an innovative cellulose based environment friendly hydrogel was experimentally synthesized as an alternative to acrylate-based synthetic hydrogels for personal care product and other absorption purposes. The cellulose based hydrogels were prepared by free radical graft copolymerization reaction of cotton with acrylic acid (AA) and acrylamide (AM) using N,N-methylene-bis-acrylamide (MBA) as a crosslinker in the presence of initiator potassium persulphate ($K_2S_2O_8$) system. The maximum water absorption capacity of the prepared hydrogels were 50 g/g in deionized water. Optimized preparation condition was investigated depending on monomer concentration, initiator concentration, crosslinker concentration, pH, time and temperature for equilibrium water absorption which were 120%, 10%, 5%, 7, 2h and 50°C respectively. For structural characterization FTIR spectroscopy, SEM analysis, TGA and XRD technique were performed. The result ensure that the characteristic of prepared hydrogel can be effectively used in personal absorbent products, tissue engineering, biomedical application etc. and as adsorbent material in polluted water treatment.

Key words: Cellulose, Hydrogels, Water absorption, Graft copolymer, Crosslinker.

INTRODUCTION

According to definition, hydrogels are such crosslinked polymeric substances that remain insoluble and can hold large amount of fluid compared to its body mass[1]. Crosslinking may be done either chemically or mechanically. Hydrogel research has spent more than 3 decades but its research interest has not affected, more over the understanding level about structure, properties, potential uses has increased enough. Super absorbents (SAPs) are commercial member of hydrogel family. Due to higher water absorbency of hydrogels it can be used in personal healthcare[2,3], agriculture [4], biomedical application [5], construction [6], and other industrial applications[7,8]. The available hydrogels are completely petroleum-based and polyelectrolytic gels, as a result it has large impact on environment. Recent trend of polymeric materials is to be biodegradable so that they will be harmless for the health and environment. In this regard scientists have gained enough success by incorporating cellulose, starch[9], chitosan[10], proteins[11] and

carrageenan[12,13] in polymeric chains. Cellulose is most abundant and ubiquitous natural polymer in this planet. Not only in the present time but also from ancient time cellulose was using in industry and other various applications[14].In combination with cellulose and other synthetic polymers composite hydrogel can be synthesized with specific properties[15,16].Polymers with functional groups in its structure exhibits substantial response towards natural stimuli (pH, temperature, ionic yield, concentration, presence of enzyme etc.) and swell or shrink respectively. This swell-shrink behaviour has profound effect on the multi-disciplinary applications and can be controlled by altering methods of preparation. Among different methods of hydrogel preparation radical copolymerization technique is the most widely used due to its simple reaction path and less expensive instruments. In radical copolymerization monomers are copolymerized in presence of initiators and crosslinker and grafted on cellulosic materials. In this study hydrogel was synthesized following techniques described in [17] by copolymerization reaction of cotton with acrylic acid (AA) and acrylamide (AM) using N,N-methylene-bis-acrylamide (MBA) as a crosslinker in the presence of initiator potassium persulphate ($K_2S_2O_8$).This study deals with effects of different process parameters on the water absorption of cotton hydrogel to determine the optimum conditions for preparation and characterization of the internal structure of the prepared sample using modern analytical tools-SEM, FTIR, XRD and AAS. In addition metal ions uptake by the synthesized hydrogel was also investigated so that it can be use as filtering media in multilayer filtration system in water treatment plant[18,19].

EXPERIMENTAL

Materials

Cotton was collected from local market. It was cut into small pieces, washed with deionized water and dried. Necessary chemicals were purchased and they were of analytical grade.

Prehydrolysis and pulping

Cotton was prehydrolysed using sulfuric acid (15 ml, 1.5 % w/v) at 100°C for 3h. The material was filtered, washed with distilled water till neutrality and dried. The prehydrolysed material (1 g, based on dry weight) was pulped using sodium hydroxide (17.5 % w/v, 50 ml) at 100°C for 3 h. The resulting pulp was filtered in each case and washed with distilled water copiously till neutrality and dried at ambient temperature.

Preparation of cotton-g-Poly(AA-co-AM) hydrogels

Cotton-g-poly (acrylamide-acrylic acid) hydrogels were synthesized by free radical graft copolymerization of cotton with AA and AM in presence of an initiator $K_2S_2O_8$ and a crosslinking agent (MBA). In a typical sample preparation 0.5g of cotton pulp immersed in 15 ml of distilled water in three necked flask fitted with magnetic stirrer, a reflux condenser and a nitrogen line at 55°C for bubbling oxygen free nitrogen for 30 min before starting reaction. Initially 0.05g of initiator (10% w/w, based on dry cotton weight) was dissolved and added to the cotton solution with stirring for 10 min to create radicals. The total volume of the solution was controlled to 20 ml. Thereafter 0.6 g of AM (120% w/w, based on dry cotton weight) and 0.56 g of AA (120% w/w, based on dry cotton weight) were added and the mixture was stirred for 30 min. Then the reaction was proceeded for 2 h more. At the end of the reaction the prepared hydrogels were removed carefully and washed with distilled water for several days. Again the hydrogels was washed several

times with pure ethanol for dewatering and immersed in NaOH solution for hydrolysis for 24 h. Finally the hydrogel was washed with distilled water and dried in oven for 24 h at 50 °C [20].

CHARACTERIZATION

Water absorbency of hydrogels

To measure water absorbency pre-weighed sample was immersed in distilled (about 12 h) water and weighed again to remove surface water by gently dabbing with tissue paper. The water absorbency was calculated by the equation:

$$[Q_{eq} = (M_{eq} - M_o) / M_o] \quad (1)$$

Where, M_o is weight of dry hydrogel, M_{eq} is the weight of wet hydrogel at equilibrium and Q_{eq} is the water absorbency in g/g.

Determination of gel content

For the determination of gel content certain amount of hydrogel samples dried to constant weight were immersed in distilled water for 24 h to remove sol fraction. Then swell samples were taken out from the distilled water and dried to constant weight in an oven. The gel content was calculated as follows:

$$\text{Gel content (\%)} = \frac{W_g}{W_i} \times 100 \quad (2)$$

Where, W_g is the weight of dry gel after extraction in water and W_i is the initial weight of dry gel.

FT-IR analysis

FT-IR of the pure cotton, hydrolyzed cotton and hydrogels were conducted by a FTIR spectroscope (Model: FTIR-8900, Shimadzu, Japan) for the observation of functional groups present in samples within the frequency range from 400 to 4000 cm^{-1} by the method of transmission. Finely ground samples were mixed with KBr and pressed to form a KBr pellet.

Morphology and crystallinity of hydrogels

Surface morphology and crystallinity of the prepared hydrogels was observed by SEM and XRD analysis. The sample was examined by Scanning Electron Micrograph (Hitachi, Model-S3400 N, VP SEM, Japan). The micrographs were taken at a magnification of 3000 and 5000 times using (15 kV) accelerating voltage.

Effect of pH on the swelling behavior

Buffer solution at different pH was used to determine the water absorbency of hydrogels at different pH using Eq.1.

Water retention capacity at different temperature

The synthesized hydrogels were immersed in distilled water at different temperature (5°C, 25°C and 35°C) and absorption of water was determined by the Eq.1. Then the swelled samples were kept at that temperature and reweighed at different time interval. The result was presented graphically.

Adsorption of metal ions

Amount of adsorbed metal ions were calculated by immersing certain amount of synthesized non-hydrolyzed hydrogels in separate solutions (100 ml) containing 200 ppm of Cu^{2+} and Cr^{3+} with stirring at 100 rpm for 3 h. After filtration the concentration of the

filtrate was determined by Atomic Absorption Spectrometry (AAS). The amount of metal ion adsorbed by the hydrogel was expressed by the following Eq. 3.

$$q_e = \frac{(C_0 - C_e) \times V}{W} \quad (3)$$

Where, C_0 and C_e are the concentration of metal solution of initial and after adsorption by the hydrogel respectively, and V is the volume of metal solution and W is the weight of dry hydrogel sample. The result expressed in amount of metal ion per gram of dry hydrogel sample.

RESULTS AND DISCUSSION

Effect of reaction conditions on synthesis and water absorption

Figure 1 shows the effects of different reaction conditions for synthesis of hydrogels and dependency of water absorption capacity. The graft yield of the hydrogel at different temperature was displayed in Figure 1a. The graft yield was maximum at 50 °C. Figure 1b shows water absorbency of hydrogel against monomer concentration. It indicates that water absorbency increases up to certain concentration of monomer as hydrophilic nature of cotton increases by grafting with hydrophilic monomer AA and AM on the backbone of cotton. Again water absorbency decreases due to accumulation of the monomer closer to polymer backbone resulting homopolymer formation over grafting. The optimum concentration of monomer was 120 % of cotton weight. The maximum water absorbency found in this case was 50 g/g. This explanation fits the literature in [7].

Figure 1c shows the effect of pH on water absorption of hydrogels in aqueous medium. Water absorption is less at lower and higher pH values. At about pH value 7 (neutral medium) water absorption was the highest. When pH value more than 4.0, ionization of $-\text{COOH}$ groups occurred and repulsion of NH_3^+ groups enhanced water absorbency. Again in low alkaline medium repulsion of $-\text{COO}^-$ enhances water absorbency and water absorption decreases with increasing

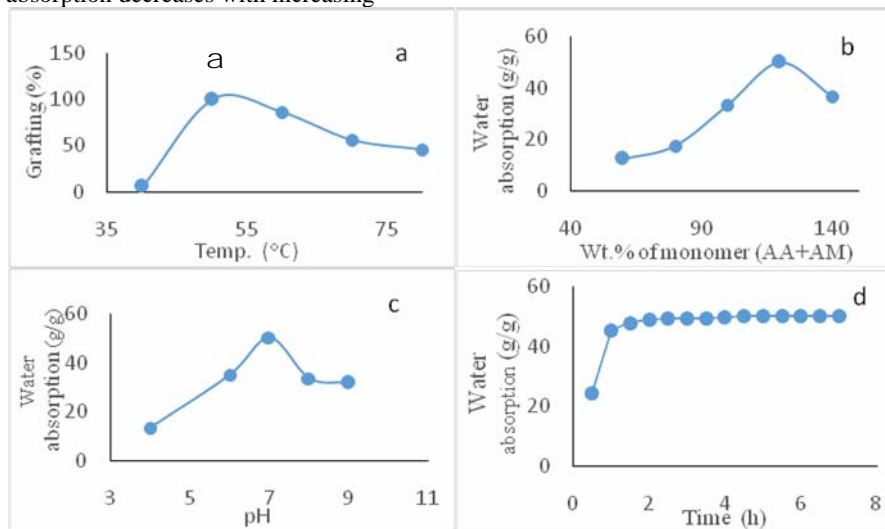


Figure 1. The effects of different reaction conditions for synthesis of hydrogels and water absorption.

pH. Maximum water absorbency shows at pH value 6 to 8 which is a indication of the pH sensitivity of the hydrogel[21].

Another important character of hydrogels is equilibrium water absorbency and it was shown in Figure1d. It shows that almost 80% of absorbed water was taken by hydrogel sample within 1h which indicates that the material can be used in personal absorbent product.

Characterization of the synthesized Cotton-g-Poly(AA-co-AM)

Among three FTIR spectra in Figure 2, a new band is present in spectrum 2c which is an indication of grafting of monomer on the cotton backbone. A peak at 1667 cm^{-1} is a shift of C=O in stretching vibration, caused by superposition of C=O in amide I and C=O in COO⁻ [22]. The new peak at 1570 cm^{-1} corresponds to the asymmetric -COO⁻ stretching vibration.

When comparing the X-ray diffraction patterns of raw cotton and hydrogels from Figure 3 it can be observed that the broad peaks at 15° and 22° diffraction angles were shorten in Figure 2b and its smaller peak intensity showed that grafting reaction reduced the crystallinity of cotton.

Figure 4 shows the SEM images of raw cotton and hydrogels. The raw cotton has a smooth and continuous fibre surface while hydrogels have rough and discontinuous puffed surface. The porous surfaces of hydrogels helps water diffusion in the polymeric network, thereby producing high swelling capacity in the hydrogels.

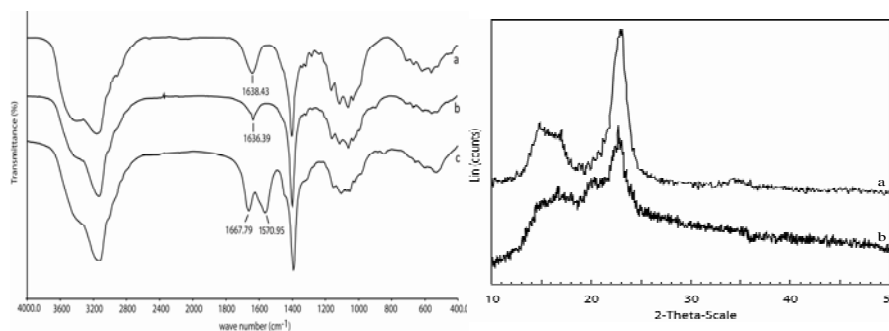


Figure2. FTIR spectra of (a) raw cotton, (b) Hydrolysed cotton and (c) Hydrogels

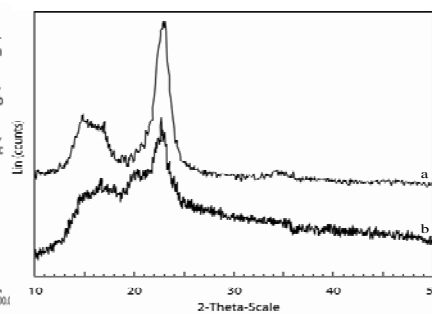


Figure3. Diffraction of (a) raw cotton and (b) Hydrogels

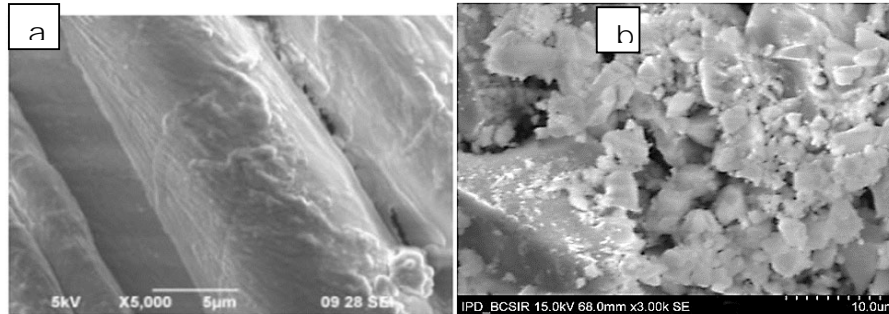


Figure4. SEM images of (a) raw cotton and (b) Hydrogels

Water Retention measurement

Water holding capacity of hydrogel is a significant property to use as absorbent. Water retention capacity was determined at various temperature and showed in Figure 5. The results showed that synthesized hydrogel can hold water for about two days. The holding capacity of water decreases with increasing temperature. Water retention capacity was determined at three different temperatures (5, 25 and 35°C). At higher temperature water holding capacity decreases due to rupture of hydrogen bonds [23].

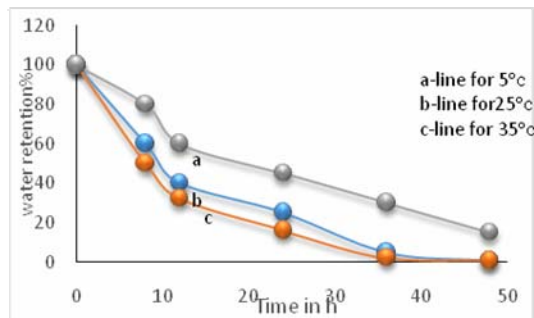


Figure5. Water retention capacity of Cotton-g-Poly(AA-co-AM) hydrogel at different temperatures.

Metal ions uptake

A solution of Cu^{2+} and Cr^{3+} ions with different concentration was prepared and a weighted small amount of dry hydrogel sample was put into the beaker containing the ionic solutions. After stirring for 3 h the sample got coloured, which indicates that the hydrogels can absorb colour from solution. The ions taken by the hydrogel were 353mg/g and 255mg/g for Cr^{3+} and Cu^{2+} respectively. This is due to the difference in ionic radii of the ions. The smaller the ion size more chance to enter into the pore of hydrogel[24].

Mechanism for the preparation of Cotton-g-Poly(AA-co-AM) hydrogels

The final hydrogel products were prepared by graft copolymerization of acrylic acid and acrylamide onto hydrolysed cotton in presence of KPS as a free radical initiator and MBA as a cross linking agent. The suggested mechanism for the preparation of hydrogel is given below:

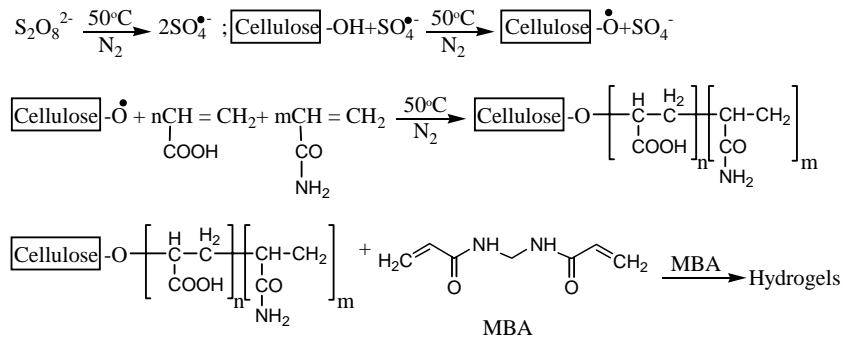


Figure 1. Suggested mechanism for the preparation of Cotton-g-p(AA-co-AM) hydrogels. According to the proposed mechanism KPS produces sulfate anion radicals which reacts with hydroxyl groups of cotton to form more active macroradicals. The macroradicals attacks the monomers (AA and AM) to propagate a polymeric chain and thereafter become free radical donor to neighboring molecule to enlarge grafted chain. The polymeric chain simultaneously react with MBA and crosslinked structure is formed. The mechanism of hydrogels preparation is similar with those proposed in the literature [25, 26].

CONCLUSIONS

The new green absorbent (Hydrogels) were synthesized by grafting acrylic acid (AA) and acrylamide (AM) onto backbone of hydrolysed cotton in presence of a crosslinker N,N-methylene-bis-acrylamide (MBA) and initiator potassium per sulphate (KPS) using free radical graft copolymerization technique. As the hydrogel shows moderate water retention capacity, so it can be used as absorbent for agriculture in arid area. It has also a promising possibility of use in personal health care products. Further studies is required for the kinetic study of metal ions absorption by the hydrogel which will provide useful information about the suitability of using the synthesized product for the treatment of waste water.

References

- [1] Bao Y, Ma J and Li N, "Synthesis and swelling behaviors of sodium carboxymethylcellulose-g-poly(AA-co-AM-coAMPS)/MMT superabsorbent hydrogel," *Carbohydrate Polymer*, Vol. 84(1), pp. 76-82, 2011.
- [2] Sadeghi M and Hosseinzadeh H, "Synthesis of Starch-Poly (Sodium Acrylate-co-Acrylamide) Superabsorbent Hydrogel with Salt and pH-Responsiveness Properties as a Drug Delivery System," *Journal of Bioactive and Compatible Polymers*, Vol. 23(4), pp. 381-404, 2008.
- [3] Maithili K and Ram M, "Disposable diapers: A hygienic alternative," *Indian Journal of Pediatrics*, Vol. 70(11), pp. 879-881, 2003.
- [4] Zohuriaan-Mehr MJ, Omidian H, Doroudiani S and Kabiri K, "Advances in non-hygienic applications of superabsorbent hydrogel materials," *Journal of Material Science*, Vol. 45(21), pp. 5711-5735, 2010.

- [5] Thomas V, Yallapu MM, Sreedhar B, Bajpai SK, "A versatile strategy to fabricate hydrogel-silver nanocomposites and investigation of their antimicrobial activity," *Journal of Colloid and Interface Science*, Vol. 315(1), pp. 389-395, 2007.
- [6] Song FX, Wei JF and He TS, "A method to repair concrete leakage through cracks by synthesizing super-absorbent resin in situ," *Concrete and Building Materials*, Vol. 23(11), pp. 386-391, 2009.
- [7] Pourjavadi A, Barzegar Shand Zeidabadi F, "Synthesis and properties of biodegradable hydrogels of K-carrageenan grafted acrylic acid-co-2-acryl amido-2-methyl propane sulfonic acid as candidates for drug delivery systems," *Reactive and Functional Polymers*, Vol. 67(7), pp. 644-654, 2007.
- [8] Kashyap N, Kumar N and Kumar M, "Hydrogels for Pharmaceutica and Biomedical Applications," *Critical Reviews in Therapeutic Drug Carrier Systems*, Vol. 22(2), pp. 107-149, 2005.
- [9] Li A, Zhang J, and Wang A, "Utilization of starch and clay for the preparation of superabsorbent composite," *Bioresource Technology*, Vol. 98, pp. 327-332, 2007.
- [10] Shang J, Shao Z and Chen X, "Electrical behavior of a natural polyelectrolyte hydrogel: chitosan/carboxymethylcellulose hydrogel," *Biomacromolecules*, Vol. 9, pp. 1208-1213, 2008.
- [11] Pourjavadi A and Salimi H, "New protein-based hydrogel with superabsorbing properties: effect of monomer ratio on swelling behavior and kinetics," *Industrial Engineering Chemistry Research*, Vol. 47, pp. 9206-9213, 2008.
- [12] Rasool N, Yasin T, Heng JYY and Akhter Z, "Synthesis and characterization of novel pH-, ionic strength and temperature-sensitive hydrogel for insulin delivery," *Polymer*, Vol. 51, pp. 1687-1693, 2010.
- [13] Hubbe MA, Ayoub A, Daystar JS, Venditti RA and Pawlak J, "Enhancement absorbent products incorporating cellulose and its derivatives: A review," *BioResources*, Vol. 8(4), pp. 6556-6629, 2013.
- [14] Eichhorn SJ, Dufresne A, Aranguren M, Marcovich NE, Capadona JR, Rowan SJ, Weder C, Thielemans W, Roman M, Renneckar S, Gindl W, Veigel S, Keckes J, Yano H and Abe K, "Current international research into cellulose nanofibres and nanocomposites," *Journal of Material Sciences*, Vol. 45(1), pp. 1-33, 2010.
- [15] Liang XT, Huang ZQ, Zhang YJ and Liu ZJ, "Synthesis and properties of novel superabsorbent hydrogels with mechanically activated sugarcane bagasse and acrylic acid," *Polymer Bulletin*, Vol. 70(6), pp. 1781-1794, 2013.
- [16] Chen H and Fan MJ, "Novel thermally sensitive pH-dependent chitosan/carboxymethyl cellulose hydrogels," *Journal of Bioactive and Compatible Polymers*, Vol. 23(1), pp. 38-48, 2008.
- [17] Chang C, Lue A and Zhang L, "Effects of crosslinking methods on structure and properties of cellulose/PVA hydrogels," *Macromolecular Chemistry and Physics*, Vol. 209(12), pp. 1266-1273, 2008.
- [18] Krusic MK, Milosavljevic N, Debelkovic A, Uzum OB and Karadag E, "Removal of Pb²⁺ ions from water by poly(acryl amide-co-sodium methacrylate) hydrogels," *Water air Soil Pollutants*, Vol. 223(7), pp. 4355-4368, 2012.
- [19] Ahmed AEI, "Hydrogels for water filters: Preparation and antibacterial evaluation," *Journal of Applied Polymer Science*, Vol. 122(2), pp. 1162-1167, 2011.

- [20] Marc G, Mele G, Palmisano L, Pulit P and Sannino A, "Environmentally sustainable production of cellulose-based superabsorbent hydrogels," *Green Chemistry*, Vol. 8, pp. 439-444, 2006.
- [21] Yin YH, Jia XM, Dong H, Ying Y and Zheng H, "Study of the swelling dynamics with other shooting effect of hydrogel based on sodium alginate-g-acrylic acid," *Carbohydrate Polymer* Vol. 71(4), pp. 682-689, 2008.
- [22] Wu F, Zhang Y, Liu L and Yao JM, "Synthesis and Characterization of a novel cellulose-g-poly(acrylic acid-co-acrylamide) superabsorbent composite based on flax yarn waste," *Carbohydrate Polymer*, Vol. 87(4), pp. 2519-2525, 2012.
- [23] Roy A, Bajpai J and Bajpai AK, "Dynamics of controlled release of chlorpyrifos from swelling and eroding biopolymeric microspheres of calcium alginate and starch," *Carbohydrate Polymer*, Vol. 76(2), pp. 222-231, 2009.
- [24] Boyed EG, Schubert J and Adamson AW, "The exchange adsorption of ions from aqueous solutions by organic zeolites. I. Ion-exchange equilibria," *Journal of American Chemical Society*, Vol. 69(11), pp. 2818-29 1947.
- [25] Pourjavadi A, and Salimi H, "New protein-based hydrogel with superabsorbing properties: effect of monomer ratio on swelling behavior and kinetics," *Industrial & Engineering Chemistry Research*, Vol. 47, pp. 9206-9213, 2008.
- [26] Rashidzadeh A, Olad A, Salari D and Reyhanitabar A, "On the preparation and swelling properties of hydrogel nano composite based on sodium alginate-g-poly(acrylic acid-co acrylamide)/clinoptilolite and its application as slow release fertilizer," *Journal of Polymer Research*, Vol. 21(2), pp. 344-359, 2014.