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Synthesis, characterization and swelling properties of poly (acrylic acid)/Zr-pillared clay superabsorbent composites

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Abstract

Superabsorbents hydrogel were prepared by using Zr pillared- montmorillonite KSF by graft copolymerization reaction of acrylic acid (AA). Swelling behavior of pillared clay based superabsorbent films in distilled water and different pH values were investigated at room temperature. It was also obtained that pillared clay based superabsorbents were pH dependent and showed a reversible swelling behavior. Water absorbency of pillared clay based superabsorbent (PILC-SA) was increased by decreasing pillared clay amount in the network of the superabsorbents. SEM and XRD analysis were conducted for further characterization of the PILC-SA. XRD revealed the basal spacing of the pillared clays before and after in-situ incorporation indicating that the morphology of the superabsorbent was exfoliated and the layers of clay dispersed on the composite.

Keywords: *Pillared clay, superabsorbent composite, swelling.*

Poli(akrilik asit) / Zr-Sütunlu kil süper absorplayıcı kompozitlerin sentezi, karakterizasyonu ve şişme özellikleri

Özet

Süperabsorplayıcı hidrojeller Zr sütunlu montmorillonit KSF ile akrilik asitin (AA) aşı kopolimerizasyon tepkimesi ile hazırlandı. Sütunlu kil tabanlı superabsorplayıcı filmlerin şişme özellikleri oda sıcaklığında destile edilmiş suda ve farklı pH değerlerinde araştırıldı. Sütunlu kil tabanlı süperabsorplayıcıların pH duyarlı ve yenilenebilir şişme özelliği olduğu bilgisine de ulaşıldı. Sütunlu kil tabanlı

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süperabsorplayıcıların (PILC-SA) su absorplaması süperabsorplayıcının yapısındaki sütunlu kilin miktarının azalmasıyla artmaktadır. SEM ve XRD analizleri PILC-SA'ların karakterizasyonları için gerçekleştirildi. Sütunlu killerin etkileşime girmeden önce ve sonraki tabakalar arası mesafesine XRD ile bakılarak superabsorplayıcıların morfolojisinin değiştiği ve kilin tabakalarının kompozit üzerinde dağıldığı ortaya çıkarıldı.

Anahtar kelimeler: *Sütunlu kil, süperabsorplayıcı kompozit, şişme.*

1. Introduction

Pillared clays are layered materials prepared by the exchange of compensating cations for oligomeric or polymeric hydroxymetals, followed by calcination. The calcination promotes the dehydration and dehydroxylation of the polycations, with the formation of metal oxides that act as pillars, maintaining the separation between the layers with the appearance of interlayer and interpillar spaces with molecular dimensions [1-4]. The first step in the pillaring process is to prepare a pillaring agent. Zr-pillared clays (Zr-PILCs) were prepared from zirconyl chloride solutions. For synthesis of pillared clay catalysts, Montmorillonite KSF (KSF) was used as precursor material. In this study, zirconium pillared montmorillonite KSF samples were prepared for synthesis poly (acrylic acid)/Zr-pillared clay superabsorbent composites. Clays, such as kaolin [5], montmorillonite [6, 7], attapulgite [8], mica [9], bentonite and sercite [10], have all been used for the preparation of superabsorbent composites. To our knowledge, Zr-pillared clays have not been reported as additive of superabsorbents. This approach for the preparation of superabsorbent composites is beneficial owing to develop mechanical and materials properties because of negative features such as high production cost and low gel strength. Additionally, clays have been more suitable for use in water absorbents as additives because of their hydrophilic nature.

Superabsorbents are loosely crosslinked polymeric networks that can absorb and retain aqueous fluids up to thousands of times their own weight [11]. Since the US Department of Agriculture reported the first superabsorbent polymer [12], much attention has been drawn to improve performances of superabsorbents in the past several decades [13-15]. Superabsorbents are used widely in many fields, such as feminine napkins, disposable diapers, agriculture, etc., [16-20] where water retention ability of superabsorbents is critically important.

The present article deals with the synthesis and characterization of Zr-PILC and Zr-PILC containing acrylic based superabsorbent hydrogel composites. Moreover the performance of inorganic filler amount on the properties of the superabsorbents was compared each other in detail. The swelling characteristics of superabsorbent composites in distilled water were studied. The influence of pH value on water absorbency in water was also investigated. Additionally, the synthesis and the characterization of pillared clays containing acrylic-based superabsorbent hydrogel composites were carried out by XRD, FT-IR, and SEM.

2. Materials and method

Acrylic acid (AA) monomer and the crosslinker N, N′-methylene–bisacrylamide (MBA) purchased from Fluka were used without further purification. Ammonium persulfate (APS), sodium metabisulfite (SMBS) and potassium hydroxide (KOH) (all from Merck) were used as received.

Montmorillonite KSF (KSF) supplied from Fluka Company was utilized as precursor material of Zr-PILC. Chemical composition of Montmorillonite KSF is 55.0% SiO_2, 18.0% Al_2O_3, 4.0% Fe_2O_3, 3.0% MgO, %3.0 CaO, <0.5% Na_2O, 1.5% K_2O, 5.0% Sulphate and 10.0% loss on ignition. KSF has a surface area of 20-40 m^2/g. BET surface area (S_{BET}) of Zr- KSF was obtained from N_2 adsorption– desorption isotherms at 77 K, measured on SORPTOMATIC 1990 after a degassing under vacuum for 3 h at 150 ºC by using MILES-200 Advanced Data Processing Sorption Software Version 3.00. Zr- KSF has a surface area of 117.5 m^2/g.

2.2. Synthesis of Zirconium pillared montmorillonite KSF (Zr-KSF)

Zr-KSF was prepared from zirconyl chloride solution. In a first set of preparation, 0.2 M $ZrOCl_2$. 8 H_2O solution was previously refluxed at 95 °C for 5 and 24 h. The solution re- fluxed for 5 h remained limpid, but it turned turbid after refluxing for 24 h. The solutions were added dropwise to 2 wt% (%50 acetone %50 H_2O) suspension of KSF at a rate of 10 mequiv. Zr g^{-1} clay. The final suspensions were stirred for 24 h at room temperature. Samples were further aged for 10 days. The pillared clays were washed by dialysis and oven-dried. After this period, the samples were calcined at 250 °C for 2 h.

2.3. Preparation of the superabsorbent composite

The poly (acrylic acid)/Zr-pillared clay superabsorbent composites were synthesized through the graft copolymerization of acrylic acid on pillared clay with MBA as a crosslinker and APS as an initiator in an aqueous solution. The inorganic pillared clay particles in the network acted as additional network points [21]. Acrylic acid (20 g) was neutralized with potassium hydroxide solution (12.1 g KOH +10.0 g H_2O). After the neutralization, MBA solution (0.013 g MBA + 3.0 g H_2O) was added to the monomer solution. The mixture was poured into a 600-mL beaker, which was equipped with a magnetic stirrer and thermometer. 0.05, 0.10 and 0.20g of Zr-KSF were added to monomer solutions and stirring was continued until homogeny mixtures were obtained. To start polymerization reaction, the APS solution (0.05 g APS +1.5 g H_2O) and the SMBS solution (0.063 g SMBS + 2g H_2O) were added to the mixture. The temperature of mixture was increase rapidly to almost 100°C within a few minutes. Prior to hardening the products, the mixtures were pour into the Petri dish to obtain thin films. Samples were dried in a vacuum oven at 70°C for 24 h and then a few amount of water was dropped to film and after 1 h, the film was removed from Petri dish and dried again.

2.4. Measurement of water absorbency

Water absorbency measurement was performed weighing dry sample (m_0) and water-swollen sample at time t (m_t) at room temperature, respectively. The percent of swelling values were determined from the following equation [22].

$$\%Swelling = 100\left[\frac{(m_t - m_0)}{m_0}\right] \tag{1}$$

The swelling measurements were made thrice and the average data was used for calculations.

2.5. Measurement of the swelling rate

Dry film superabsorbents composite samples were firstly weighed and then immersed in 20 mL of distilled water at room temperature. The weighing swelling ratios of samples were performed at various times. The swelling ratios of superabsorbents were calculated by eq. (1). Swelling equilibrium times were determined via this process.

2.6. Characterization of pillared clays and Zr-KSF based superabsorbents

Fourier transform infrared (FTIR) spectra were recorded on a FTIR Perkin Elmer Spectrum BX-II in the 4000–400 cm^{-1} region using KBr pellets for pillared clays and ATR probe for superabsobent films. Morphology of the samples was examined using a Jeol JSM 60 SEM operating at the accelerating voltage of 20 kV after coating the sample with a gold film. X-ray powder diffraction patterns were obtained by Rigaku Dmax 2200/ PC model instrument with Cu K radiation (40 kV, 40 mA). XRD measurements of superabsorbents were performed by film form. For clays and pillared clays, analysis was process to powder form. The change of clay layer space by pillaring and preparing superabsorbents was found out by means of Bragg equation $(2d\sin\theta = n\lambda)$. XRD reveals the basal spacing of the pillared clays before and after in-situ incorporation, indicating the morphology of the superabsorbent (exfoliated, intercalated or only dispersed).

3. Results and discussion

3.1. Swelling rate measurements

Figure 1 displays the swelling rate of Zr-KSF based superabsorbents. It was found that the swelling ratio of superabsorbent hydrogel containing 0.05g of Zr-KSF was higher than superbsorbents containing 0.10 and 0.20g of Zr-KSF at swelling equilibrium, respectively. Additionally,the swelling rate of Zr-KSF (0.05g)-SA was the highest than the others and the time needing to reach swell equilibrium increases with increase of pillared clay amount. Zr-KSF based superabsorbents reached equilibrium within 80 min. The percentages of equilibrium swelling values were at about 10285 for Zr-KSF (0.05g)-SA, at about 9850 for Zr-KSF (0.10g)-SA and at about 9440 for Zr-KSF (0.20g)-SA. This may be attributed to crosslink density and elasticity of polymer network. Pillared clay act as crosslinking points because of carrying –OH groups in their structure. The carboxylate groups of the polyacrylate chains may react with -OH groups of pillared clays. Increasing the amount of pillared clays in the polymeric network resulted in the generation of more crosslink points that increase the crosslink density of the composite, and then the elasticity of the polymer chains decrease. It was deduced that more crosslink points may occur between Zr-KSF (0.20g) pillared clay and SA. Shortly, the superabsorbent with lower pillared clay content had a higher initial swelling rate and higher water absorbency and required less time to reach swelling equilibrium.

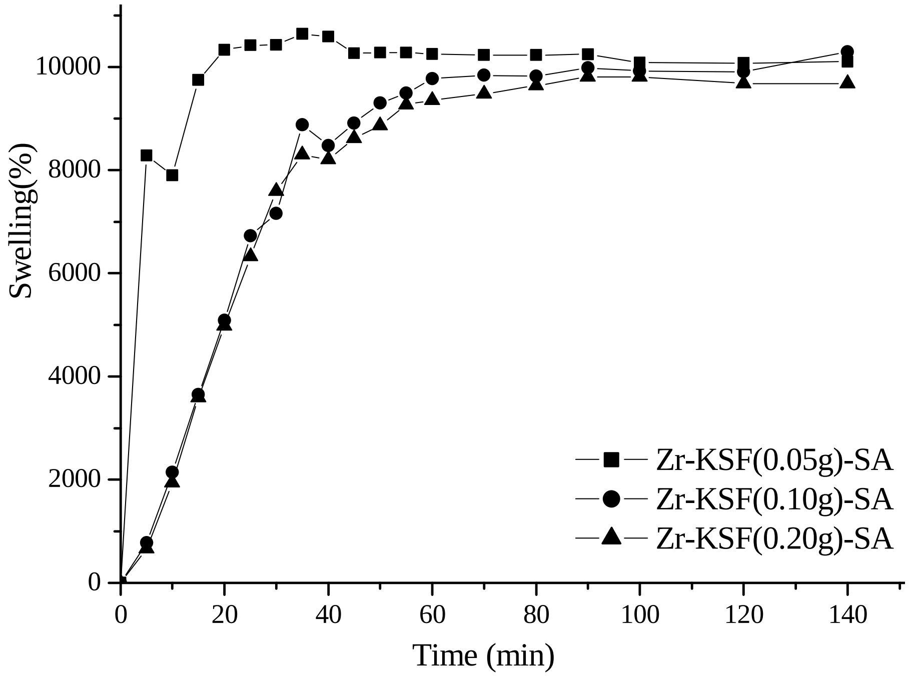

Figure 1. Swelling kinetics of superabsorbents composite in distilled water.

3.2. pH-sensitivity of the superabsorbents

To clarify pH sensitivity of pillared clay based superabsorbents, firstly the films were immersed in distilled water and then in different buffer solutions until swelling equilibrium. Figure 2 showed the effect of the pH on water absorbency of superabsorbents. The buffer solutions at pH 3.4, 4.0, 6.7 and 8.5 were prepared by using citric acid and $Na_2HPO_4.2H_2O$ solutions. The absorbency of the superabsorbent composite increased sharply as the pH increased from 3.4 to 8.5. The superabsorbent composites were sensitive to the pH change. Shrinkage was occurred at acidic pH for all Zr-KSF based superabsorbents. The change in the swelling ratio by changing pH may be explained by Lee and Wum suggestion [23]; in an acidic environment, the $–COO^-$ groups on the polymeric chains turn into –COOH groups, while the –COOH groups on the polymeric chain turn into $–COO^-$ groups in basic solutions, and this behavior was interpreted as a buffer action of –COOH and $–COO^-$. In the acidic environment, the repulsion between polymeric chains decreases, which leads to the decrease of water absorbency. The –COOH groups present within the network remain almost nonionized, thus imparting almost non-polyelectrolyte type behavior to the hydrogel [22]. Furthermore, there exist H-bonding interactions between carboxylic groups of acrylic acid and amide groups of acrylamide. These H-bonding interactions result in the formation of a compact or tight structure which does not permit much movement of polymeric chains within the hydrogel network, which lead to minimum swelling of hydrogel [22]. The ionization of the carboxylic acid groups of the gel occurred. More hydrophilic polymer was occurred at higher pH value because of ionization of the carboxylic acid group and contributed to the higher water absorption. As seen in Figure 2, the swelling behavior of Zr-KSF based superabsorbent films seem to be pH dependent. The content of pillared clay in the network of the superabsorbent affected the swelling ratio. More shrinkage and lower swelling was obtained by increasing the content of Zr-KSF in the polymeric network. Additionally, crosslinking might be increased in order of increasing the amount of pillared clay. The water content decreased due to increased level of crosslinking [24].

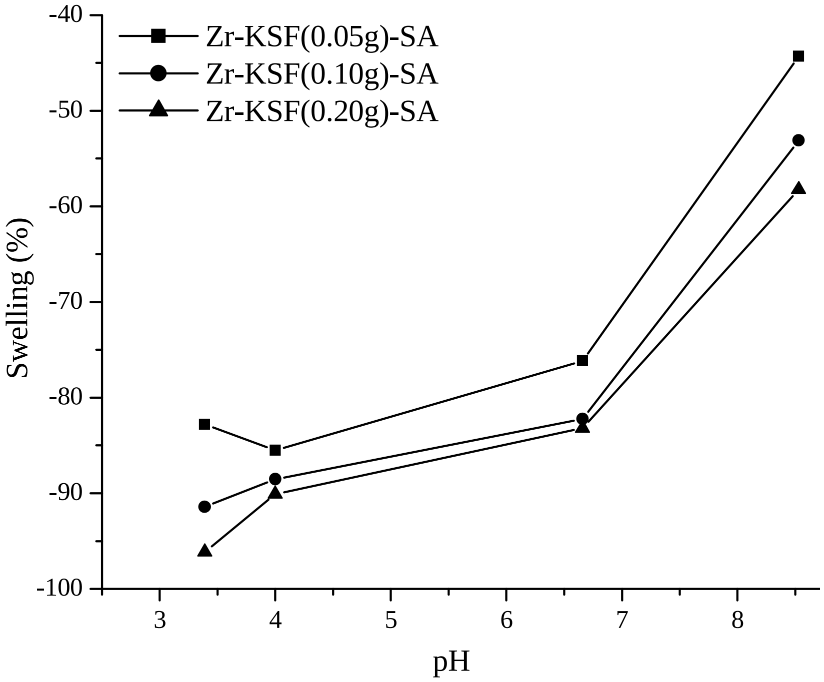

Figure 2. Effect of pH on the equilibrium swelling of superabsorbents.

3.3. Swelling reversibility of superabsorbents

To reveal swelling reversibility, the Zr-KSF based superabsorbents were equilibrated at pH=1.2, and then alternated between solutions at pH=7.4 and pH=1.2 for about 120 minutes, respectively. A swelling was measured at about 900% for Zr-KSF (0.05g)-SA, 537% for Zr-KSF (0.10g)-SA and 540% for Zr-KSF (0.20g)-SA at pH= 7.4, respectively. Then the films put into pH=1.2 for 120 min. and approximately 3.50%, 0.60% and 23.0% deswellings for Zr-KSF(0.05g)-SA, Zr-KSF(0.10g)-SA and Zr-KSF(0.20g)-SA, respectively were determined. It was also clearly seen from Figure 3. Besides, when the superabsorbent films altered from acidic to basic buffer and then to acidic buffer, pillared clay based superabsorbents showed a reversible swelling behavior with relatively fast response. Zr-KSF (0.05g)-SA had the fastest response to pH change. It can be added that reversible swell-shrink properties of pillared clay based superabsorbents would be beneficial characteristics for pH sensitive systems with controllable swelling ability. Also, this result indicates that the PAMA composite can be used as a recyclable water-managing material for the renewal of arid and desert environment [25].

3.4. SEM images

The SEM micrographs of Zr-KSF, Zr-KSF (0.05g)-SA, Zr-KSF (0.10g)-SA and Zr-KSF (0.20 g)-SA were exhibited in Figure 4. A considerable difference was observed between pillared clay and superabsorbents. Polymeric network was predominant in superabsorbent hydrogel morphology. When the content of pillared clay was increased, the surface of polymeric network was affected, the signs of pillared clay were increased and surface of hydrogels were less smooth. Also SEM micrographs were supported the homogeneity of composed superabsorbents after graft polymerization had been occurred. Homogenous dispersion of pillared clay particles may be contributed to more crosslinking structure. Furthermore more crosslinking might be obtained by increasing pillared clay amount in the superabsorbents. SEM micrographs of superabsorbents clearly represented lower swelling capacities because of their highly rigid type structure.

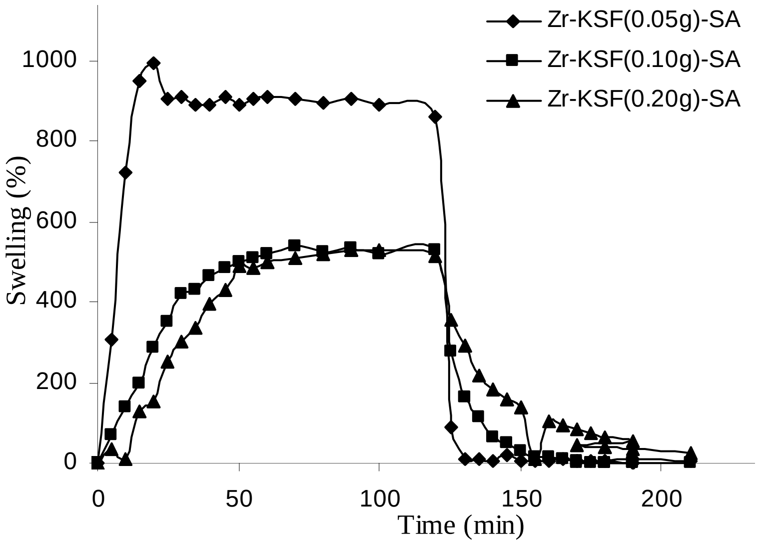

Figure 3. pH-dependent reversible swelling behavior of superabsorbents (Superabsorbents equilibrated at pH=1.2, then alternated between solutions at pH=7.4 and pH=1.2).

3.5. FT-IR Analysis

These IR characteristic bands of clay were observed and only little shifts of were noticeable in pillared clays and the network of pillared clay based composites from Table1. The little shifts of these all bands showed that the basic clay layer structure remains unaffected on pillaring and polymerization. These results suggested that the pillaring agents physically entrapped within the PILC structure.

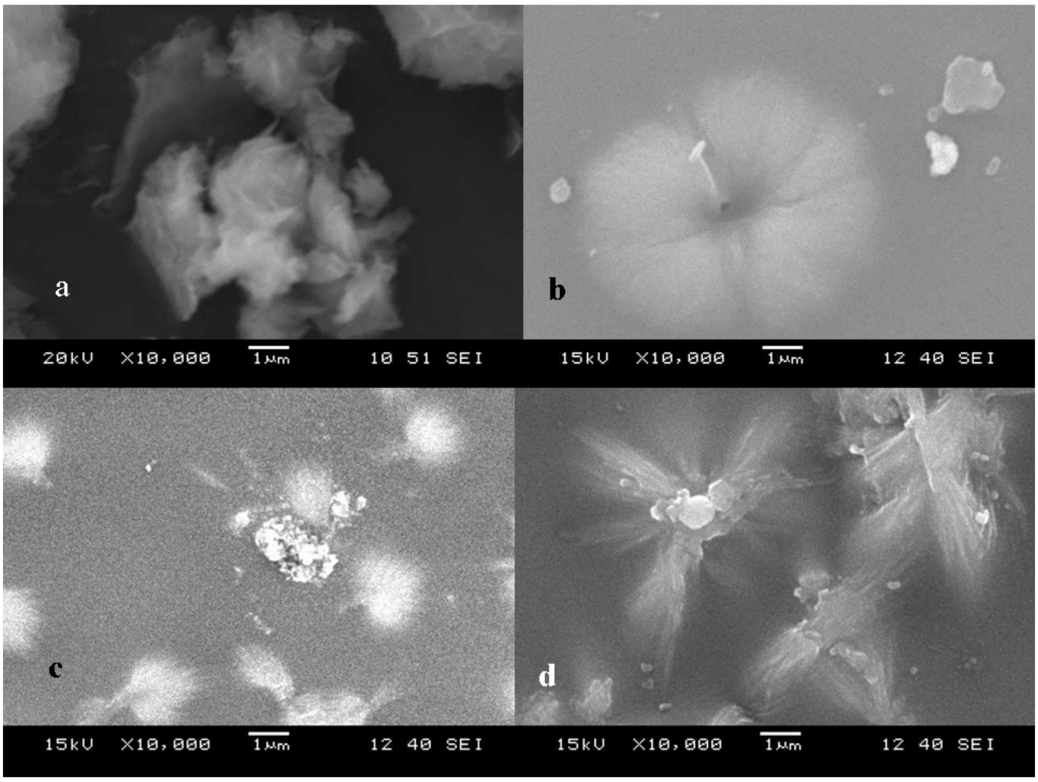

Figure 4. SEM micrographs of (a)Zr-KSF (b)Zr-KSF(0.05g)-SA (c)Zr-KSF(0.10g)-SA (d) Zr-KSF(0.20g)-SA (10000x magnification).

Table 1. The characteristic FT-IR data of the samples.

IR bands(cm^{-1})	**Samples**				
	KSF	**Zr-KSF**	**Zr-KSF (0.05g)-SA**	**Zr-KSF (0.10g)-SA**	**Zr-KSF (0.20g)-SA**
Al_2OH(octahedral layer)	3619	3626	3642	3647	3633
Streching vibrations of H_2O	3411	3429	3395-3345	3395-3345	3395-3345
Stretching vibration of $–CH_2$			2985-2879	2988-2881	2984-2883
Stretching vibration of C=O			1754	1750	1747
Bending vibrations of H_2O	1636	1630	1683	1682	1675
Asymmetric vibration of R-COOK			1542	1539	1543
Bending vibration of $–CH_2$			1470	1463	1469
Symmetric vibration of R-COOK			1408	1402	1406
Asymmetric streching vibrations of SiO_2 tetrahedra	1046	1044	1076	1076	1065
Bending vibrations of Al_2OH	917	921	915	915	917
	842	843	799	800	820
Bending vibration of Si-O	524	525	524	524	526
	468	469	470	469	472

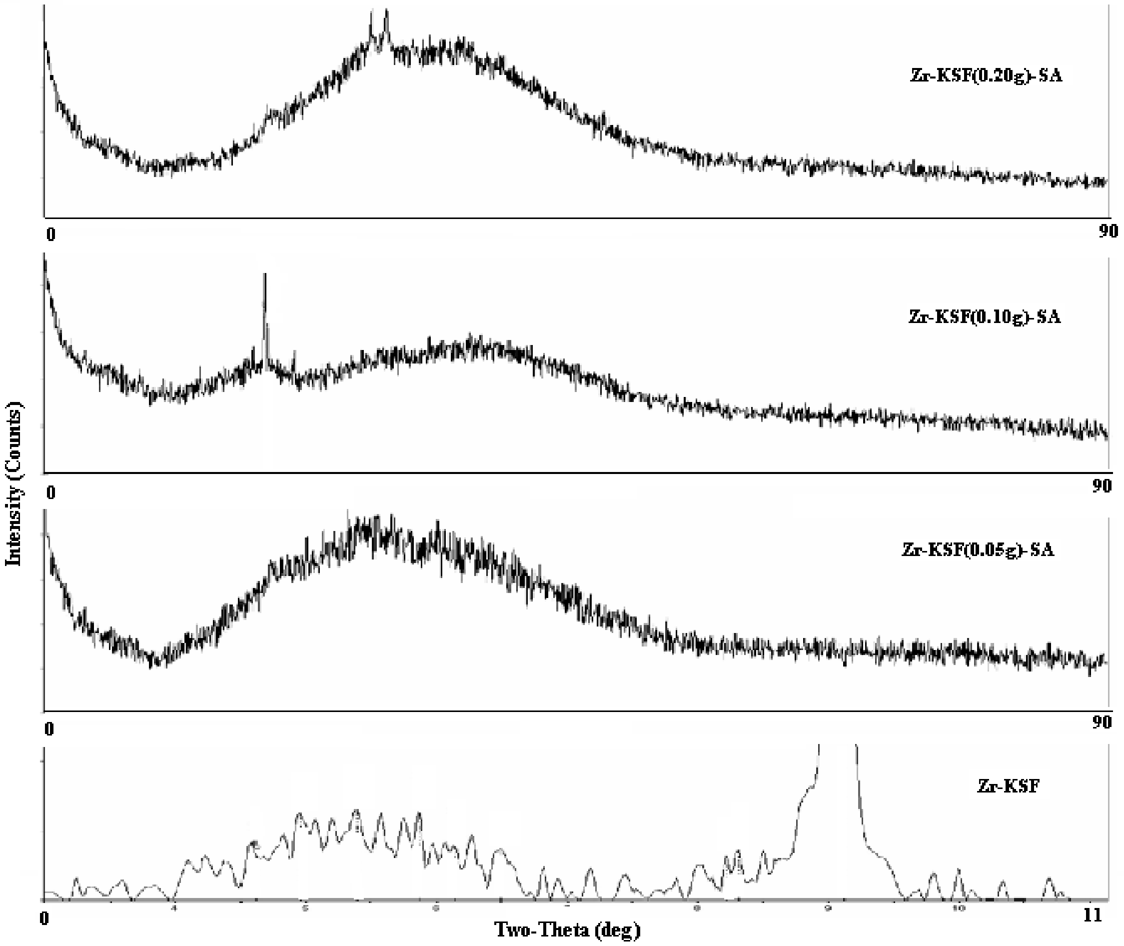

Figure 5. XRD patterns of Zr-KSF; Zr-KSF (0.05g)-SA; Zr-KSF (0.10g)-SA and Zr-KSF(0.20g)-SA.

3.6. XRD analysis

The X-ray diffraction patterns of Zr-KSF, Zr-KSF (0.05g)-SA, Zr-KSF (0.10g)-SA and Zr-KSF (0.20g)-SA were shown in Figure 5. The lattice spacings of montmorillonite

KSF and Zr pillared KSF were 12.55Å at 2θ=6.99° and 19.13Å at 2θ=4.60°, respectively. 001 lattice spacing of KSF was increasing by pillaring with Zr polyoxications. After polymerization with pillared clays the diffraction peak corresponding to the montmorillonite (d_{001} basal spacing of montmorillonite layers) was not observed at about 2θ=5.0-6.0°. The absence of this peak indicates that the montmorillonite layers are exfoliated or highly expanded. The expansion mechanism probably originates from the growing polymer chains by adsorbed monomers on the clay layers pushing apart the layers even in high clay loadings [26]. Layers of montmorillonite were completely dispersed in a continuous polymer matrix as single layers. The XRD patterns Zr-KSF based composites showed two crystal peaks at 2θ of ~ 20° and 30°, respectively. These data support the presence of layers of clays. The graphs of superabsorbents indicated that sharp crystal peaks were observed when the content of Zr-KSF was increased. Composites reflected more amorphous character.

4. Conclusion

In this study, swelling characters of composites were revealed out after grafting occurred between pillared clays and the acrylic network. It was found that swelling degree and fast response to pH change of the pillared clay based superabsorbent hydrogels was decreasing by increasing the content of the pillared clay in the network of the hydrogel. The swelling rate of Zr-KSF (0.05g)-SA was higher than Zr-KSF (0.10 g)-SA and Zr-KSF (0.20 g)-SA. Additionally, the time needed to reach swelling equilibrium decreased with decrease of pillared clay content. The swelling values of superabsorbents were significantly increased with the raise of pH in the range 3.4 -8.5.

FTIR analysis and SEM micrographs impressed that the pillared clay based superabsorbents were successfully obtained. Besides, XRD analysis of the samples showed that layers of montmorillonite were exfoliated in the hydrogel structure and were completely dispersed in a continuous polymer matrix as single layers.

Clays and pillared clays might be added to superabsorbent hydrogel to compose economic products. Modifying of poly (acrylic acid) composites with inorganic materials affected the swelling character and product cost. Decreasing of swelling ratio was observed by increasing the content of pillared clay. All Zr- KSF based poly (acrylic acid) composites were pH sensitive. The behavior of shrinkage at acidic and swelling at basic environment was useful for pH sensitive systems with controllable swelling ability such as controllable drug delivery. Also, the character of water absorbing and swelling reversibility was indicator of suitable applications in agriculture and horticulture.

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