EFFECTS OF OPERATING CONDITIONS ON WATER ABSORPTION CAPACITY OF SUPERABSORBENT HYDROGELS

by

Noun Abdelwahab

A Thesis presented to the Faculty of the
American University of Sharjah
College of Engineering
In Partial Fulfillment
of the Requirements
for the Degree of

Master of Science in
Chemical Engineering

Sharjah, United Arab Emirates

April 2018

Approval Signatures

We, the undersigned, approve the Master's Thesis of Noun Abdelwahab.

Thesis Title: Effects of Operating Conditions on Water Absorption Capacity of Superabsorbent Hydrogels

Signature **Date of Signature**
(dd/mm/yyyy)

___________________________ _______________

Dr. Naif Darwish
Professor, Department of Chemical Engineering
Thesis Advisor

___________________________ _______________

Dr. Ahmed Aidan
Senior Lab instructor, Department of Chemical Engineering
Thesis Co-Advisor

___________________________ _______________

Dr. Paul Nancarrow
Associate Professor, Department of Chemical Engineering
Thesis Committee Member

___________________________ _______________

Dr. Yehya El-Sayed
Associate Professor, Department of Biology, Chemistry and Environmental Sciences
Thesis Committee Member

___________________________ _______________

Dr. Naif Darwish
Head, Department of Chemical Engineering

___________________________ _______________

Dr. Ghaleb Husseini
Associate Dean for Graduate Affairs and Research
College of Engineering

___________________________ _______________

Dr. Richard Schoephoerster
Dean, College of Engineering

___________________________ _______________

Dr. Mohamed El-Tarhuni
Vice Provost for Graduate Studies

Acknowledgement

First and foremost, I would like to thank ALLAH for giving me the strength, patience, and knowledge to complete this work.

I would like to express my gratitude and appreciation to my advisor Dr. Naif Darwish and Co-advisor Dr. Ahmed Aidan, for their guidance, patience and encouragement throughout this research. I am thankful to Dr. Yehya El Sayed and Mr. Ziad Sara for their help and training in conducting the FTIR analysis. Special thanks to my committee members, Dr. Paul Nancarrow and Dr. Yehya El Sayed, for their valuable feedback. I also would like to thank the Chemical Engineering Department in the American University of Sharjah for the graduate teaching assistant provided to me over the course of my graduate study. I wish to thank my family, specially my parents, for their love, sacrifices and support throughout my life. Last but surely not least, I am deeply grateful to my (second) father Elmoeiz Elahmadi for his love, encouragement, and advice.

Dedication

To my family…

Abstract

Superabsorbent hydrogels are three-dimensional networks of hydrophilic polymers that have an extraordinary ability to absorb and retain water. Therefore, they have been utilized in many applications such as disposal diapers, drug delivery, and water desalination. In this study, the effects of environmental and synthetic parameters on the absorbency of superabsorbent hydrogels are investigated using a two-level factorial design. Commercial hydrogels were used to examine the effects of temperature, swelling time, pH, and hydrogel amount, whereas synthesized poly acrylamide hydrogels were used to study the effects of monomer, cross-linker, and initiator concentrations. Moreover, both commercial and synthesized hydrogels were characterized using Fourier transform infrared (FTIR) spectroscopy. Higher absorbency is obtained for the commercial hydrogels by increasing the swelling time from two to eight hours. A reduction of 2.8 g/g (g water/g hydrogel) was observed by increasing the level of pH from 8.5 to 10. Water absorption capacity of the hydrogel increased by 14.72 g/g upon increasing the temperature by 8.5^{o}C above room temperature. For the synthesized hydrogel, it was found that increasing monomer concentration by 5% reduces absorbency by 2.51 g/g, whereas increasing cross-linkers concentrations from 0.5% to 1.75% decreases the absorbency by 3.01 g/g. Increasing the concentration of the initiator by 0.2% was found to improve absorbency by 0.98 g /g. The results show that time, temperature, and monomers have positive effects on absorbency while pH, cross-linkers and initiators reduce it.

Keywords: ***Hydrogels; absorbency; two-level factorial design; poly acrylamide hydrogels; commercial hydrogels***

Table of Contents

List of Figures

List of Tables

List of Abbreviations

AA	Acrylic Acid
AAm	Acrylamide
APS	Ammonium persulfate
FTIR	Fourier Transform Infrared
IPN	Interpenetrating Network Polymeric hydrogels
LCST	Lower Critical Solution Temperature
MBA	N,N-methylenebisacrylamide
NIPM	N-isopropylacrylamide
PSA	Poly (Sodium Acrylate)
PVA	Polyvinyl alcohol
SPS	Sodium Persulfate
TEMED	N,N,N`,N`-tetramethylethylenediamine
W_i	Initial Weight of Hydrogels (g)
W_f	Final Weight of Hydrogels (g)

Chapter 1. Introduction

Hydrogels are three-dimensional networks that consist of one type or more of polymer chains, which are linked together chemically or physically [1-3]. The affinity of hydrogel to water makes it an interesting material in the fields of biomedical, agricultural and tissue engineering [3]. The high capacity of absorbing water comes from the hydrophilic groups that are attached to the backbone of polymer chains inside hydrogels [4]. According to Chirani et al. [4] the hydrogel term appeared for the first time in the literature to describe a colloidal gel of inorganic salts in 1840. Wichterle and Limwere [4] produced poly hydroxyethylmethacrylate (pHEMA) hydrogel which was the first material to be used in the human body [4]. Based on the groups that are incorporated into their backbones, hydrogels can be anionic, cationic or neutral [5]. Figure 1.1 shows the integral parts of the hydrogels which are monomers, cross-linkers and initiators [6]. Monomers are the small molecules that have ability to join together to form polymers [7]. The initiators are the chemicals that break the unsaturated bonds inside monomers to convert them to radical monomers to start polymerization [7]. The cross-linkers are the materials that connect the chains of polymers to each other [7].

Superabsorbent hydrogels can absorb and retain huge amount of water. Acrylic acid, its salt and acrylamide are the most used monomers in preparing superabsorbent hydrogel. Many studies have been done on developing and improving their absorbency. The effects of the different parameters on their absorbency have been investigated in many papers. These parameters have been classified into synthetic and environmental parameters. The synthetic parameters are such as the concentration of crosslinkers, initiators and monomers. On other hand, the ionic strength, temperature and pH of medium are the most studied environmental parameters [8]. To the best knowledge of the present author, most of the published studies in the literature investigated the effects of synthetic or environmental parameters independently without any consideration for their interaction effects.

The main aims of this work are to: 1) study the main (single) and interaction effects of environmental parameters on the absorbency of commercial hydrogels using two-level factorial design, and 2) examine the main and interaction effects of synthetic parameters on the absorbency of prepared poly acrylamide hydrogels using two-level factorial design. The environmental parameters include hydrogel amount, swelling time, pH and temperature. While monomer, cross-linker and initiator concentrations are the investigated synthetic parameters.

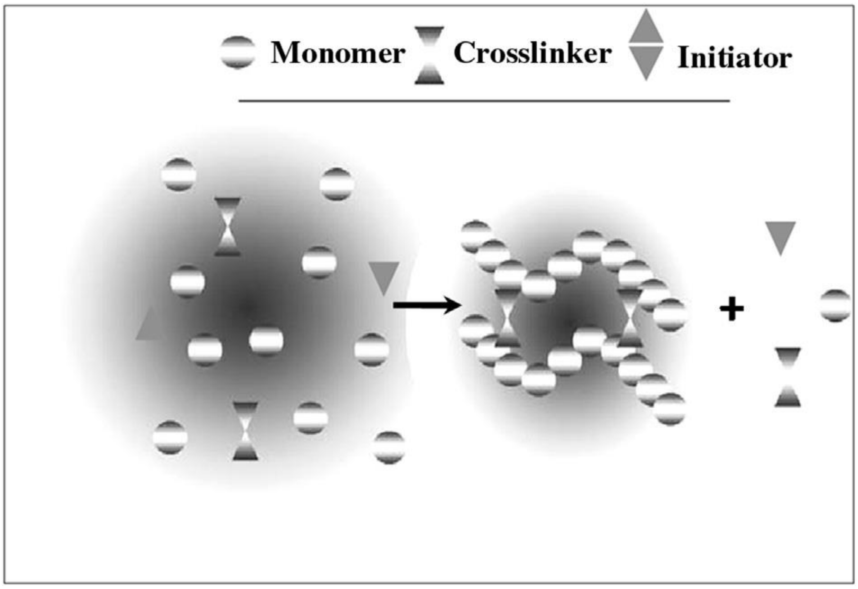


Figure 1.1: Integral parts of hydrogels [6].

Chapter 2. Background and Literature Review

In this chapter, the classifications, synthesis, properties, and applications of hydrogels are presented. Moreover, previous studies on superabsorbent hydrogels, their synthesis, and the parameters affecting their absorbency are discussed.

2.1. Classifications of Hydrogels

The hydrogels could be classified according to their origin, structure, electrical charge, absorbency and sensitivity.

Based on origin, the hydrogels could be natural or synthetic. The natural ones are such as proteins (collagen and fibrin) and polysaccharides (chitosan and dextran) [5]. They are used in delivering drug and wound dressing for their biodegradability and biocompatibility [5]. On the other hand, they have low mechanical strength and high degradation rate [6].

The synthetic hydrogels are made from different type of monomers using various methods. The main advantage of this kind of hydrogels is the ability of controlling the final properties of produced hydrogels by playing on the type and the concentration of their ingredients as well as the method of manufacturing. Monomers like vinyl acetate, acrylamide, ethylene glycol and lactic acid can be used to produce this kind of hydrogels. The hydrogels could also be made by combining the synthetic and the natural monomers [9].

According to structure, the hydrogels could be homopolymer, copolymer, multipolymer and interpenetrating networks.

Homopolymer are synthesized from one type of monomers as depicted in Figure 2.1. The hydrogels of this type will carry the properties of their monomers [5].

Figure 2.1: Homopolymer hydrogel [5].

Copolymer hydrogels consist of two types of monomers [5]. They carry the properties of the monomers that form them. For example, adding 2-hydroxyethyl methacrylate (HEMA) to acrylic acid (AA) will produce absorbent hydrogels with good mechanical properties [9]. The monomers inside copolymers could be arranged in different ways to form alternating, block, graft or random copolymers as shown in Figure 2.2 [5].

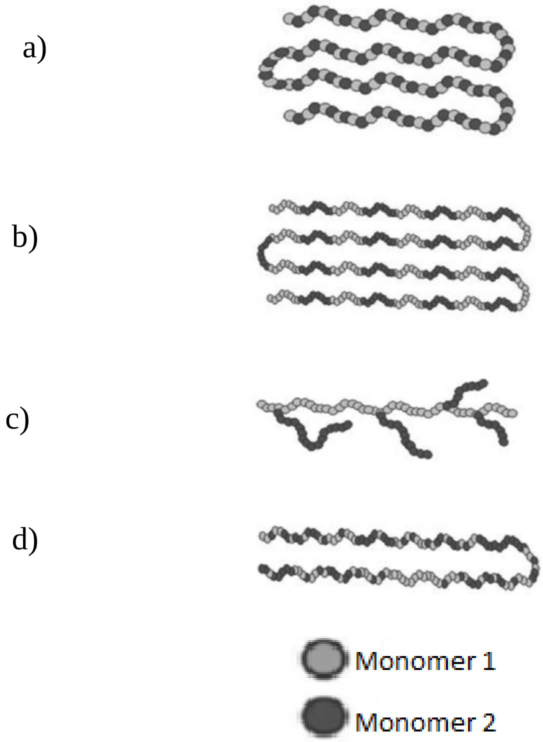


Figure 2.2: The different forms of copolymeric hydrogels. a) alternating copolymer hydrogels, b) block copolymer hydrogels, c) graft copolymer hydrogels d)Random copolymer hydrogels [5].

Multipolymer hydrogels are produced from three or more types of monomers [5]. For example, adding a third monomer like N-isopropylacrylamide (NIPM) to AA and HEMA, form strong absorbent thermo-responsive hydrogels [10]. Figure 2.3 demonstrates the structure of multipolymer hydrogels.

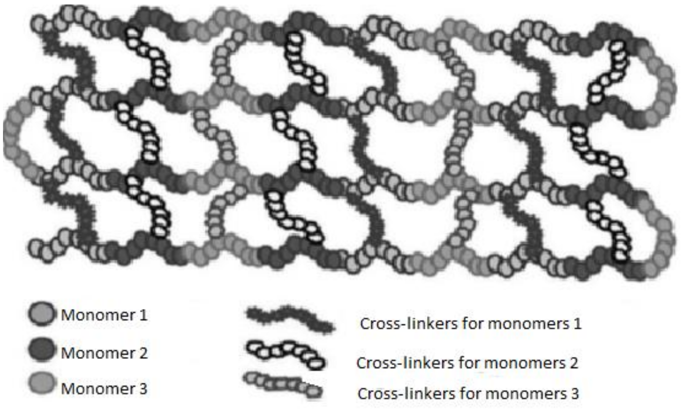


Figure 2.3: Structure of multipolymer hydrogels [5].

The chain of one type of monomer can penetrate the network of other monomer without any chemical reaction to form semi-interpenetrating network polymeric hydrogels. If one chain of polymer penetrates the chain of other polymer, the produced hydrogel is called interpenetrating network polymeric hydrogel [5]. Figure 2.4 describes the interpenetrating network polymeric hydrogels (IPN).

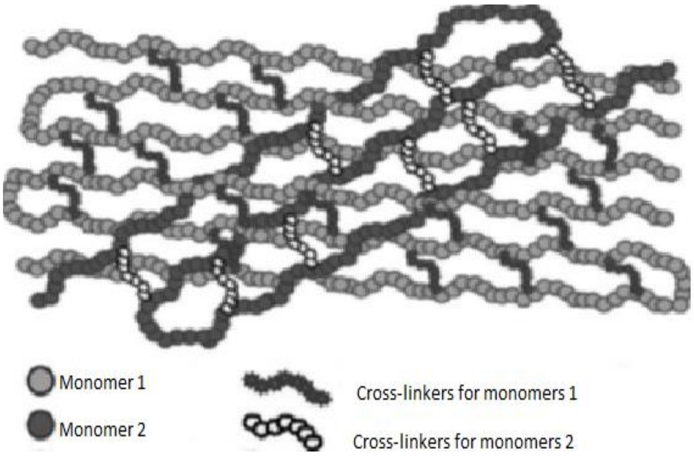


Figure 2.4: Interpenetrating network polymeric hydrogels [5].

Also, hydrogels can be classified according to the electrical charge attached to their backbone. Polyacrylamide, polyethylene glycol and poly (vinyl alcohol) are examples for the neutral hydrogels. The charged hydrogels could be ionic (acrylic acid polymers), cationic (aminoethyl methacrylate polymers) or ampholytic with negative and positive groups together [5].

From the aspect of absorbency, the hydrogels could be divided into non-absorbent hydrogels that are based on hydrophobic monomers, absorbent hydrogels which 1 g of them can absorb 1g of water and superabsorbent hydrogels that can absorb water up to 10 times of their weight [8].

Some of the hydrogels show response to the change of the surrounded conditions (pH, temperature, electric-field or light). This type of hydrogels is called smart hydrogels and have four categories, i.e., temperature-responsive, pH-responsive, electro-responsive, and light responsive [11].

Temperature-responsive hydrogels are usually made from hydrophobic monomers. However, N-isopropylacrylamide, which is a thermo-responsive hydrogel contains both hydrophobic and hydrophilic groups with 32^oC lower critical solution temperature (LCST) [12]. This kind of hydrogels absorb water when the temperature of surrounded solution is below their LCST [13]. Above this temperature, hydrogels start discharging the water that has been absorbed [14]. N,N-diethylacrylamide and dimethylamino ethyl methacrylate are also applied to produce this kind of hydrogel [15].

The charged hydrogels have high sensitivity to the pH of surrounded medium for the reactivity of the ionic or cationic groups that they hold. The repulsion between the same charges inside hydrogel increases the available spaces for retaining water. When the hydrogels are immersed in acidic or basic solutions the ionic or the cationic groups react with hydrogen ions or hydroxide ions to neutralize. The neutralization shields the ionic-ionic or cationic-cationic repulsion which reduces the available spaces of storing water. Therefore, ionic hydrogels deswell in acidic solutions while the cationic hydrogels shrink in basic solutions [16].

In the electro-sensitive hydrogels, the presence of cathode or anode usually affect the pH of the surrounded solution. Cathode raises the pH level while anode decreases it. Therefore, cationic hydrogels deswell at the presence of cathode, while ionic hydrogels contract at the presence of anode [17].

In the case of light-responsive hydrogels, exposing hydrogels that contain chromophore such as trisodium salt of copper chlorophyllin to light will affect their absorbency. This type of hydrogels absorbs the light and converts it to heat which enhances the absorbency of water for the increasing of temperature [17].

2.2. Synthesis of Hydrogels

Hydrogels consist of monomers that are connected to each other to form chains that are linked to other chains to produce networks. Networks could relate together chemically or physically to give hydrogels. Two main processes are involved in manufacturing hydrogels, i.e., polymerization to form polymers and then cross-linking the chains of polymer(s) (depending on whether one type of polymer or two types are used) [18].

Among the different types of polymerization, the free radical polymerization is the most suitable technique for producing absorbent hydrogels [4]. In the free radical polymerization, the unsaturated bond inside monomer is broken using free radical species (R*) which is produced from a compound (I). Opening the bond of one monomer will create a new radical that can break another bond for another monomer and the process will be repeated until termination [4].

After the production of polymer chains through polymerization, cross-linking is conducted to connect the polymer chains together. The type and the degree of the cross-linking affect the properties of the final produced hydrogels. The cross-linking can be carried chemically or physically [17].

In the physical cross-linking, the chains of polymer are linked physically by heating, using radiation or applying freezing- thaw cycles [17]. On the other hand, chemical cross-linking requires a chemical reaction in the presence of an agent (cross-linker) to join the different chains of polymer. Cross-linking the hydrogels chemically can be conducted by the addition of aldehydes or through the condensation reaction [17].

Chemical cross-linking by adding a chemical material is preferred in manufacturing absorbent hydrogels [3]. Some of the monomers that compose the structure of polymer chains and contain free radical species could react with the cross linkers to form networks [3]. The type of the used cross-linker is depending on the kinds of monomers involved. The applied cross-linkers are usually control the type of produced hydrogels. In the production of the homopolymer, only one type of cross-linker is utilized to link the chains of polymer, while the copolymer and the multipolymer require a multifunctional cross-linker that can reacts with all presented chains and link them together. The interpenetrating networks polymeric hydrogels are cross-linked by using a cross-linker that connects the chains of the two types of the used polymers together but does not link the chains from the same type of polymer [10]. Furthermore, cross-linkers that are used in the semi-interpenetrating networks link the chains of the first type of polymer together and with the chains of second type of polymer. But it doesn’t connect the chains of the second type polymer together [19]. The cross-linker N, N-methylenebisacrylamide (MBA) is used in manufacturing of N-isopropylacrylamine/poly(sodium acrylate) (NIPM/PSA) copolymer as well as n-isopropylacrylamine/ polyvinyl alcohol (NIPM/PVA) semi-interpenetrating networks. This refers to the ability of the MBA to connect the monomers of NIPM with the chains of PSA, and the chains of the NIPM with the chains of PVA as well as the chains of NIPM together. However, it cannot join the chains of PVA with each other [20].

2.3. Properties of Hydrogels

There are many properties that are used to feature hydrogels. The most important property for hydrogels as absorbents is the swelling property. It describes the ability of hydrogels to store water. Swelling rate and swelling capacity are used in measuring the swelling property of hydrogels. Swelling rate is the speed of absorbing, while the swelling capacity is the amount of water that can be absorbed by hydrogels. The swelling capacity can be obtained by dividing the grams of absorbed water over the grams of dry immersed hydrogels. The swelling rate is the mass of absorbed water divided by the taken time for absorption [21].

2.4. Applications of Hydrogels

Since more than 80% of produced hydrogels are invested in hygienic products, Zohuriaan-Mehr *et al.* [22], classified the uses of hydrogels into hygienic and non-hygienic.

2.4.1 Hygienic applications. Hydrogels are used in the industry of disposable diapers. The diapers are consisting from absorbent core that are sandwiched between two layers. The first layer is porous while the bottom layer is nonporous. The absorbent core was made of tissue paper and the liquid was held in the voids between the fibres of papers. To hold large amount of liquids more voids are needed and thus more papers are required which increases the volume of core. Thinner diapers have been produced after adding absorbents hydrogels to their cores. The good fitting, absorbing under load and thinner layers are the properties that have been enabled in the diapers after applying absorbent hydrogels [23].

2.4.2 Non-hygienic applications. In biomedical, hydrogels are used in production of soft lenses, delivering drugs and wound dressing. The hydrogels are used in lenses for their optical transparency, oxygen-permeability and mechanical properties. In delivering drugs, temperature or pH responsive hydrogels are loaded or injected with drugs. The drugs are released inside human body as surrounded solution diffuses inside hydrogels as shown in Figure 2.5. Moreover, hydrogel is used in wounds dressing where it manages the wounds by absorbing and retaining toxins. It is also applied as debriding agents and in the components of wound pastes care [24].

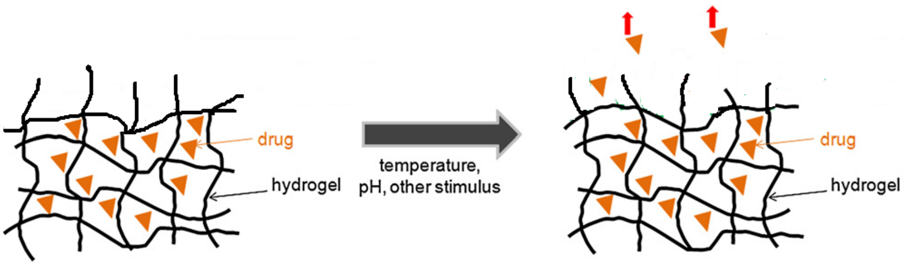


Figure 2.5: Drug Release in stimuli-responsive hydrogels [15].

In agriculture, hydrogels are mixed with soil to provide the roots of plants with moisture, in hot days, from absorbed water during irrigation. Therefore, hydrogels increase the efficiency of using water, decrease the frequency of irrigation, and stop desertification [25].

Hydrogels are applied in chicken and fish packaging to absorb water and prevent them from rotting. They are also used in meat and poultry packaging for their ability to absorb water vapour [8] and in the dressing of communication`s cables under seas or ground [8].

Recently the absorbent hydrogels have been used as forward osmosis agents in the desalination of water. The saline water is feed in one side of nano porous membrane while the other side is filled with small particles of hydrogels as depicted in Figure 2.6. The difference in osmotic presser drives the water to move to the side of dry hydrogels which absorb it. Responsive hydrogels can be used in this type of desalination to facilitate the process of dewatering [26].

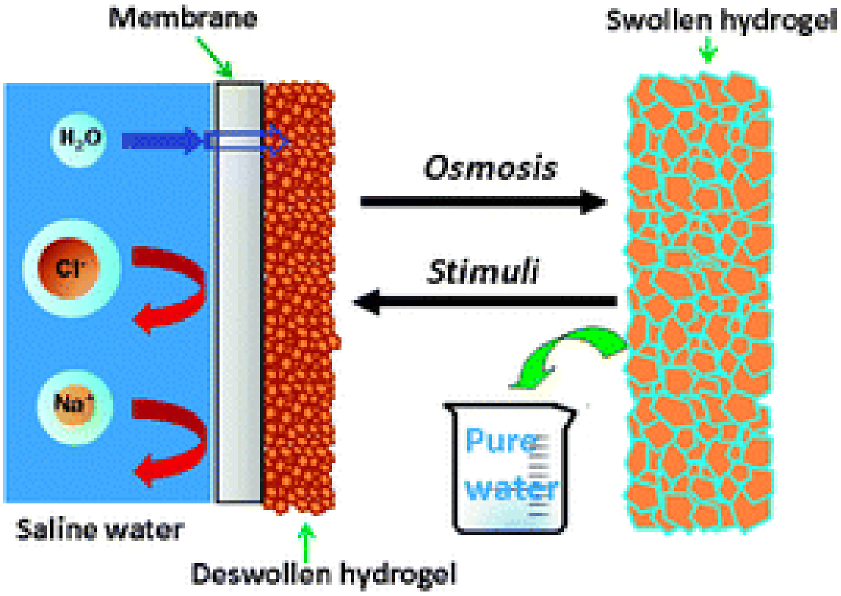


Figure 2.6: Desalination of brackish water using absorbent hydrogels [26].

Some works have been conducted to investigate the ability of hydrogels in drying natural gas and oil products such as diesel, gasoline and kerosene [27]. The water could be added to the different processes of diesel or biodiesel to remove some catalysts, soap and glycerol. Drying under vacuum or treating with salt are usually utilized in removing the water content of diesel which are difficult and consume energy. Applying the hydrogels in drying diesel has been studied by Fregolente *et al.* [27]. They reduced the water content of diesel and biodiesel samples by 80.4% and 53.3, respectively. The commercial hydrogels were used to decrease the moisture of the gasoline from 74 ppm to about 20 ppm in two hours [28].

The sensitivity of some hydrogels to environmental parameters such as temperature, pH, light or electrical charge has enabled them to be applied as sensors [29].

Absorbent hydrogels are added to some construction materials such as cement to be used in wet soils [30]. Moreover, artificial snow can be made from absorbent hydrogels by mixing them with 100 times their weight water and frozen them. Artificial snow with realistic feel will be obtained for the skiers at a temperature of 10°C [8].

2.5. Superabsorbent Hydrogels

The superabsorbent hydrogels have extraordinary ability to absorb and retain water. The most frequently used monomers in preparing superabsorbent hydrogels are acrylic acid and its salts, and acrylamide [6,31]. The superabsorbent hydrogels are usually prepared by the free-radical polymerization of monomers at the presence of cross-linkers in aqueous solution [18]. Höpfner [21] prepared poly acrylic acid hydrogels by free-radical polymerization of acrylic acid in distilled water using N,N'-methylenebisacrylamide (MBA) as cross-linkers. The polymerization was initiated by the addition of sodium persulfate (SPS) and accelerated by N,N,N',N'-tetramethylethylenediamine (TEMED). Li *et al.* [32] synthesized poly (sodium acrylate) hydrogels by free-radical polymerization of sodium acrylate. The sodium acrylate was dissolved in water before the addition of MBA (cross-linker) and ammonium persulfate (initiator). The solution was left at 70°C overnight to assure that the chains are properly cross-linked. Mahdavinia *et al.* [33] produced poly acrylamide hydrogels by free-radical polymerization of acrylamide in degassed distilled water. The MBA (cross-linker) was added to the monomer solution. Nitrogen gas was bubbled through the solution to remove any dissolved oxygen. Calcium carbonate was employed to increase the porosity of the final produced hydrogels. Ammonium persulfate (APS) and sodium metabisulfite (SMBS) were used as initiator and accelerator, respectively. The obtained gel was cut into small pieces (~2×2×2 mm) which have been immersed in ethanol for dehydration. Finally, the pieces of gel were dried overnight at 50°C.

2.6. Factors Affecting the Swelling Properties of Superabsorbent Hydrogels

The swelling properties of superabsorbent hydrogels are influenced by the polymerization reaction operating conditions and the prevailing environment of the reaction medium. These factors include ionic strength, temperature, and pH of medium and the concentration of monomers, cross-linkers, and initiators [8].

The effect of ionic strength of medium on the hydrogels absorbency was examined by Jiang *et al*. [34]. They produced poly (acrylic acid-acryl amide-2-acrylamido-2-methyl-propansulfonic acid) superabsorbent hydrogels using potassium persulfate and N,N'-methylene-bisacrylamide as initiators and crosslinkers, respectively. The effect of ionic strength was studied by changing the concentration of NaCl in the aqueous reaction medium from 1 to 1000 mmol/L. The swelling ratio decreased from approximately 700 to 58 g water/g hydrogel as the ionic strength increased from 1 to 1000 mmol/L. The presence of Na^+ neutralized the carboxylate groups inside hydrogels which decreases the ionic osmotic pressure.

Ahmed and Saeed [18] studied the effect of temperature on the absorbency of commercial poly-acrylic acid- hydrogels. The swelling ratio of these hydrogels has been examined as function of temperature and time. The rate of absorbency was high at the first two hours of immersion and then it decreased in approximately constant rate. The hydrogels reached the equilibrium with a swelling ratio of 227 g water/g hydrogel after 8 hours of immersion in 40^{o}C distilled water. The maximum swelling ratio for the same hydrogels at 30, 20 and 10^{o}C was reached after immersing the hydrogels for 12 hours. Higher temperature increased the entropy and internal energy of the hydrogel which consequently increased the diffusion process.

Lim *et al.* [35] investigated the swelling behaviour of poly acrylic acid hydrogels in a pH range of 3-11. They reported that the swelling ratio of hydrogels improved from 2 to 13 g water/g hydrogel as the pH increased from 3 to 7. Increasing the pH from 7 to 11 decreased the swelling ratio by 4 g water/g hydrogel. This has been referred to the reactivity of carboxylate ions inside hydrogel. At low level of pH, the absorbency of hydrogel decreases due to the neutralization of $-COO^-$ groups with the available cations (H^+) in the medium. Neutralizing the carboxylate ions decreases the available spaces between the strands inside hydrogel, thus reducing the hydrogel capacity to store water. As the pH increases, the repulsion between the strands inside hydrogel increases for the low amounts of cations in the medium. At pH > 7, the repulsion decreases for the effect Na^+ in neutralizing the carboxylate groups.

As to the effect of monomer concentration in general, increasing the concentration of monomers enhances the polarity of final produced hydrogels. Mohammed *et al.* [36] investigated the effect of acrylic acid concentration on the absorbency of the hydrogels that are based on acrylamide and acrylic acid. In general, it was found that the hydrogel capacity for water uptake was enhanced with higher concentration of monomers. However, Tomar *et al.*[37] found an opposite result for the effect of monomer concentration, i.e., it was found that the swelling capacity of this type of hydrogels decreases with the increasing of acrylamide concentration. For example, when the concentration of acrylamide was changed from 38.87% to 64.02% the capacity of hydrogels dropped from872 to 402 g water/g hydrogel. Increasing the amount of acrylamide resulted in a more dense structure of the hydrogel network which decreased the ability of water to penetrate the hydrogel. Singhal *et al.* [30] studied the effect of initiators and cross-linkers concentrations on the swelling ratio of the poly-acrylamide-co-acrylic acid hydrogels. The equilibrium water absorbance of the hydrogels decreased from 707 to 389 g water/g hydrogel upon increasing the content of crosslinkers from 0.0096% to 0.0385%. This has been ascribed to the strong bonds between polymer chains when high concentration of cross-linkers is applied. Increasing the concentration of crosslinkers enhanced the bonds between chains and decreases the opportunity of water to penetrate the spaces between chains. On the other hand, it was found that increasing initiator content from 0.1% to 0.5% increased the hydrogel absorbance from 302 to 573 g water/g hydrogel. The effect of initiators was explained using Flory network theory which states that water uptake capacity increases as the amount of polymer chain ends increases. Therefore, initiators enhance absorbency since it increases chain ends in networks.

In this work, the effects of the environmental and synthetic parameters on the absorbency of superabsorbent hydrogels have been investigated using two-level factorial design. Commercial hydrogels were used to examine the effects of temperature, swelling time, pH, and hydrogel amount, whereas synthesized poly acrylamide hydrogels were used to study the effects of monomer, cross-linker, and initiator concentrations. Moreover, the commercial and the synthesized superabsorbent hydrogels have been characterized using Fourier transform infrared (FTIR) spectroscopy.

Chapter 3. Results and Discussion: Commercial Hydrogels

This chapter is devoted for the investigating of environmental parameters on water absorption capacity of an available commercial hydrogel. The experiments have been designed using two-level factorial design methodology where a statistical model for the absorbency of the commercial hydrogel is developed and the results are analysed and discussed. In particular, the resulting model is used to discuss the main and interaction effects of environmental factors and the adequacy of obtained model is checked and the experimental FTIR result is discussed.

3.1. Methodology

3.1.1. Two-level factorial experimental design. Two-level factorial design has been used to study the effects of pH, temperature, swelling time and the weight of applied hydrogel. The two-level factorial design is usually applied when more than one factor is expected to affect the response (dependent) variables in the experiment under study. The strategy here is to carry out the experiment with all the factors set at one of two levels; the higher level and the lower level, and to find the main and the interaction effects of the input parameters. Determining the high and the low level for each factor is an important step in the factorial design approach. These levels are usually defined for each factor based on practical considerations [37]. The high and the low level values of each factor should not be spanning a wide range since the two-level factorial design assumes linearity of response over the range of the factor. These considerations have been considered in defining the high and the low levels of factors. The high and the low levels for each the input parameters considered in this study, i.e., hydrogel amount, swelling time, pH, and temperature, are presented in Table 3.1. The high level is denoted by +1 while the low level is denoted by -1. Based on the selected levels of the main input variables, all possible combinations of factors, together with their two-, three-, and four-level effects are shown in Table 3.2. Each run has been repeated two times to determine experimental error and the average absorbency was taken for each run. The signs of the interaction effects are obtained by multiplying the signs of related factors at each run. The main and the interaction effects of factors have been found in a form of regression model [38]. The mathematical form of the regression model for the four factors is:

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_4 x_4 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{14} x_1 x_4 + \beta_{23} x_2 x_3 + \beta_{24} x_2 x_4 + \beta_{34} x_3 x_4 + \beta_{123} x_1 x_2 x_3 + \beta_{124} x_1 x_2 x_4 + \beta_{134} x_1 x_3 x_4 + \beta_{234} x_2 x_3 x_4 + \beta_{1234} x_1 x_2 x_3 x_4 \quad (1)$$

Where: y is the response variable, which is here the water absorption capacity of the hydrogel, the betas are the main and interaction effects parameters, and x_1, x_2, x_3 and x_4 are the coded input factors. In two-level factorial designs the betas are found by taking the average of the obtained absorbencies, after multiplying each absorbency by the sign of related effect at each run. The value of β_0 represents the grand average of response variable (water absorbencies) over all runs. The input factors have been scaled to values between -1 and 1 as per the following equation:

$$x_i = \frac{Xi - \frac{Xi,_{high} + Xi,_{low}}{2}}{\frac{Xi,_{high} - Xi,_{low}}{2}} \quad (2)$$

Where X_i denotes the input parameter, i.e. hydrogel amount (A), swelling time (B), pH (C), and temperature (D), and x_i is the corresponding coded (i.e., scaled between -1 and +1).

Table 3.1: Symbols, high, and low levels of environmental factors in factorial design.

Factor	Symbol	Low Level (-1)	High Level (+1)
Hydrogel Amount (g)	A (X_1)	0.12	0.22
Swelling Time (hours)	B (X_2)	2	8
pH	C (X_3)	7	10
Temperature (ºC)	D (X_4)	23	40

The adequacy of the developed model has been checked by the normal probability plot of residuals [38], which are the values of the difference between (model) predicted water absorbency and the (experimentally) observed absorbency for each run. The residuals are ranked in ascending order and the normal probability plot for residuals have been found according to Eq. 3 [38]. The residuals have been compared to the best-fitting straight line through points. An approximate verification was made for outliers using the standardized residuals, which should fall in the range of +1 and -1, as given by Eq. 4.

$$P\% = \frac{(j - 0.5) \times 100}{n} \quad (3)$$

Where, P is the probability, j is the order of residual, and n is the number of residuals.

$$d = \frac{e}{\sqrt{MS_E}} \tag{4}$$

Where, d, e, and MS_E are the standardized error, residual and mean squared error, respectively.

The residuals have also been plotted versus the predicted absorbencies to check the adequacy of model. The median of residuals has been specified in the plot and the symmetricity of residuals around it has been observed.

Table 3.2: Factorial design matrix of input parameters (environmental parameters).

Run	**A**	**B**	**C**	**D**	**AB**	**AC**	**AD**	**BC**	**BD**	**CD**	**ABC**	**ABD**	**ACD**	**BCD**	**ABCD**
1	-1	-1	-1	-1	1	1	1	1	1	1	-1	-1	-1	-1	1
2	1	-1	-1	-1	-1	-1	-1	1	1	1	1	1	1	-1	-1
3	-1	1	-1	-1	-1	1	1	-1	-1	1	1	1	-1	1	-1
4	1	1	-1	-1	1	-1	-1	-1	-1	1	-1	-1	1	1	1
5	-1	-1	1	-1	1	-1	1	-1	1	-1	1	-1	-1	1	-1
6	1	-1	1	-1	-1	1	-1	-1	1	-1	-1	1	1	1	1
7	-1	1	1	-1	-1	-1	1	1	-1	-1	-1	1	1	-1	1
8	1	1	1	-1	1	1	-1	1	-1	-1	1	-1	-1	-1	-1
9	-1	-1	-1	1	1	1	-1	1	-1	-1	-1	1	1	1	-1
10	1	-1	-1	1	-1	-1	1	1	-1	-1	1	-1	-1	1	1
11	-1	1	-1	1	-1	1	-1	-1	1	-1	1	-1	1	-1	1
12	1	1	-1	1	1	-1	1	-1	1	-1	-1	1	-1	-1	-1
13	-1	-1	1	1	1	-1	-1	-1	-1	1	1	1	-1	-1	1
14	1	-1	1	1	-1	1	1	-1	-1	1	-1	-1	1	-1	-1
15	-1	1	1	1	-1	-1	-1	1	1	1	-1	-1	-1	1	-1
16	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1

3.1.2. Experimental absorbency test. The materials used in the experimental study include; distilled water, sodium hydroxide (NaOH) for pH adjustment, and commercial hydrogel beads which are based on acrylic acid as revealed by the FTIR spectroscopy shown in Figure 3.1 that illustrates the FTIR spectrum of the applied commercial hydrogel. The spectrum shows three main absorption peaks; at 3444.65 cm^{-1} from -OH stretching, at 2949.28 cm^{-1} from -CH stretching, and at 1664.72 cm^{-1} from -C=O stretching. These peaks confirm the network structure of poly acrylic acid [39,40].

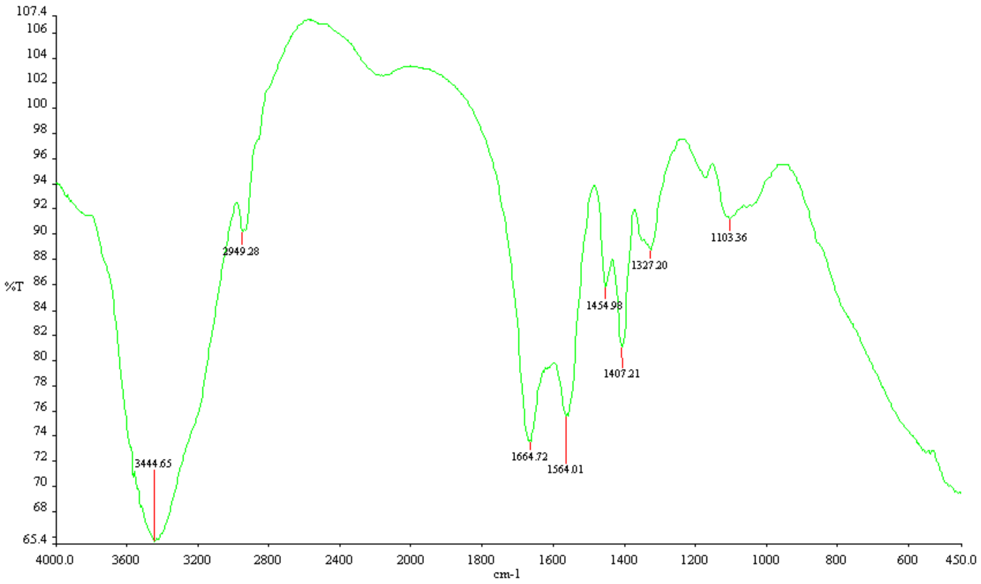


Figure 3.1: FTIR spectrum of poly acrylic acid hydrogels (commercial hydrogels).

The hydrogel beads were weighted and immersed in 50 ml of distilled water with the required level of pH that is regulated by using sodium hydroxide. A water bath (Nickel-Electro Ltd, England) has been used to keep isothermal conditions. The beads were left for a predetermined time before collecting them. The excess water wetting the external surface of the swelled beads was gently removed by using drying tissue. The weight of the swollen hydrogels was determined and the absorbency has been found using Eq. 5.

$$\text{Absorbency} = \frac{W_f - W_i}{W_i} \tag{5}$$

Where W_i is the initial weight of dry hydrogels and W_f is the weight of swollen hydrogels. Figure 3.2 shows the dry and swelled hydrogel beads.

(a)

(b)

Figure 3.2: Dry and swelled hydrogel beads. (a) dry, and (b) swelled.

3.2. Results and Discussions

The experimental absorbencies from each combination of the two-level factorial design are shown in Table 3.3.The parameters of Eq. 1 have been found as described by Eq. 6. The relations between the input and the corresponding coded variables have been defined through Eq. 2. The resulting statistical model representing the 2^4 factorial design is as follows:

$$y = 68.4 - 8.2\,\mathrm{x}_1 + 27.04\,\mathrm{x}_2 - 2.8\,\mathrm{x}_3 + 14.72\,\mathrm{x}_4 - 4.5\,\mathrm{x}_1\mathrm{x}_2 - 2.5\,\mathrm{x}_1\mathrm{x}_3 - 3.88\,\mathrm{x}_1\mathrm{x}_4 - 2.6\,\mathrm{x}_2\mathrm{x}_3 + 5.02\,\mathrm{x}_2\mathrm{x}_4 - 2.65\,\mathrm{x}_3\mathrm{x}_4 - 2.8\,\mathrm{x}_1\mathrm{x}_2\mathrm{x}_3 - 1.71\,\mathrm{x}_1\mathrm{x}_2\mathrm{x}_4 + 4.5\,\mathrm{x}_1\mathrm{x}_3\mathrm{x}_4 - 1.91\,\mathrm{x}_2\mathrm{x}_3\mathrm{x}_4 + 4.7\,\mathrm{x}_1\mathrm{x}_2\mathrm{x}_3\mathrm{x}_4 \quad (6)$$

Table 3.3: Obtained absorbencies for all conducted runs on commercial hydrogels.

Run	**Factorial Combinations**				**W$_i$ (g)**	**W$_f$ (g)**	**Absorbency (g water/g hydrogel)**	**Average of Absorbency (g water/g hydrogel)**
	A	**B**	**C**	**D**				
1	-1	-1	-1	-1	0.13	3.88	29.83	33.15
					0.12	4.21	34.58	
					0.12	4.44	35.05	
2	1	-1	-1	-1	0.23	6.97	29.88	29.07
					0.22	6.25	27.38	
					0.22	6.82	29.94	
3	-1	1	-1	-1	0.13	8.93	69.92	69.11
					0.12	8.20	68.34	
					0.12	8.63	69.08	
4	1	1	-1	-1	0.23	19.00	83.24	83.97
					0.22	18.87	84.61	
					0.22	18.74	84.05	
5	-1	-1	1	-1	0.13	4.04	31.10	33.33
					0.12	4.20	34.27	
					0.12	4.40	34.62	
6	1	-1	1	-1	0.22	7.34	33.04	31.08
					0.22	6.73	29.12	
					0.22	7.13	31.09	
7	-1	1	1	-1	0.13	11.91	93.69	96.45
					0.12	11.91	99.01	
					0.12	12.06	96.66	
8	1	1	1	-1	0.22	11.91	54.25	53.28
					0.22	11.91	52.32	
					0.22	12.06	53.28	
9	-1	-1	-1	1	0.12	7.56	61.62	57.90
					0.12	7.19	57.67	
					0.13	7.05	54.40	
10	1	-1	-1	1	0.23	10.39	45.01	46.08
					0.22	10.67	46.66	
					0.22	10.43	46.57	
11	-1	1	-1	1	0.12	17.97	147.91	147.33
					0.12	18.22	147.59	
					0.13	18.77	146.48	
12	1	1	-1	1	0.23	23.10	101.28	102.95
					0.22	23.39	103.52	
					0.22	23.04	104.05	
13	-1	-1	1	1	0.12	6.62	56.06	56.07
					0.12	6.98	56.37	
					0.12	6.89	55.77	
14	1	-1	1	1	0.23	10.31	44.25	44.18
					0.22	9.92	44.47	
					0.22	9.90	43.81	
15	-1	1	1	1	0.12	14.19	121.23	119.52
					0.12	14.71	119.88	
					0.12	14.37	117.44	
16	1	1	1	1	0.23	20.73	90.00	90.89
					0.22	20.06	90.93	
					0.22	20.49	91.73	

3.2.1. Main effects of input variables. In this section the main (single) effect of each of the four input variables is discussed. The main effects of all four input variables are displayed in Figure 3.3. In factorial design approach, the main effect of a certain input variable is represented by the value of the coefficient of that input variable as it occurs in Eq. 1, i.e., the value and the sign of β_i. For example, the main effect of the hydrogel amount ($A=X_1$) can be recognized from the value of β_1 (the coefficient of x_1) in Eq. 6, which is -8.2 as given by the model of regression (Eq. 6). This means an adverse effect of the amount of the hydrogel, i.e., increasing the coded hydrogel amount by one unit, i.e., 0.05g, decreases the absorbency of commercial hydrogels by 8.2 g water/g hydrogel. This can be ascribed to the bonding between beads during swelling, which been also reported elsewhere [41]. The water reacts as adhesive material that fills voids on the beads` surfaces and holds them together by interlocking, as shown in Figure 3.4. Increasing the hydrogel amount raises the number of surrounded beads for each bead which can bond with them at the presence of water by interlocking, a thing that can prohibit the free swelling of some beads.

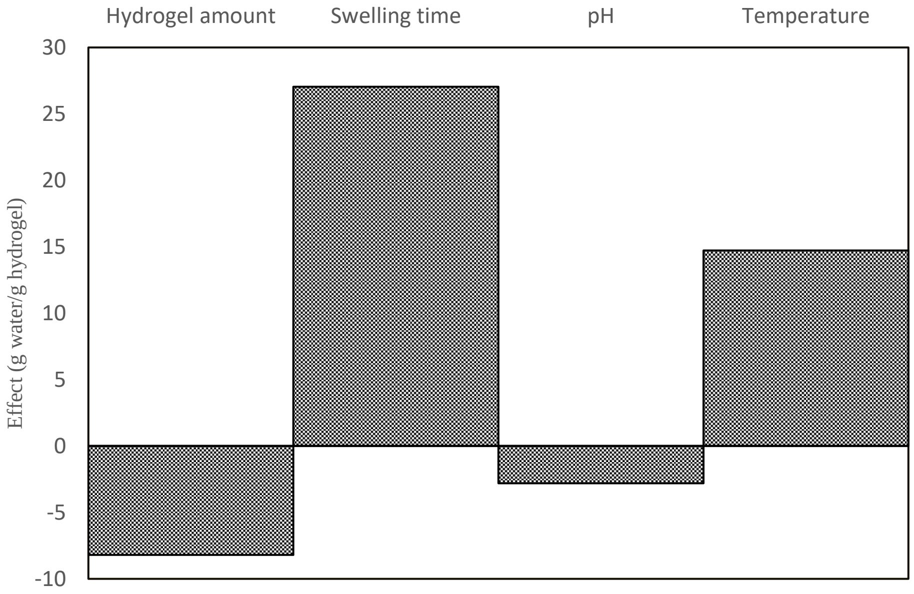


Figure 3.3: Main effects of environmental parameters.

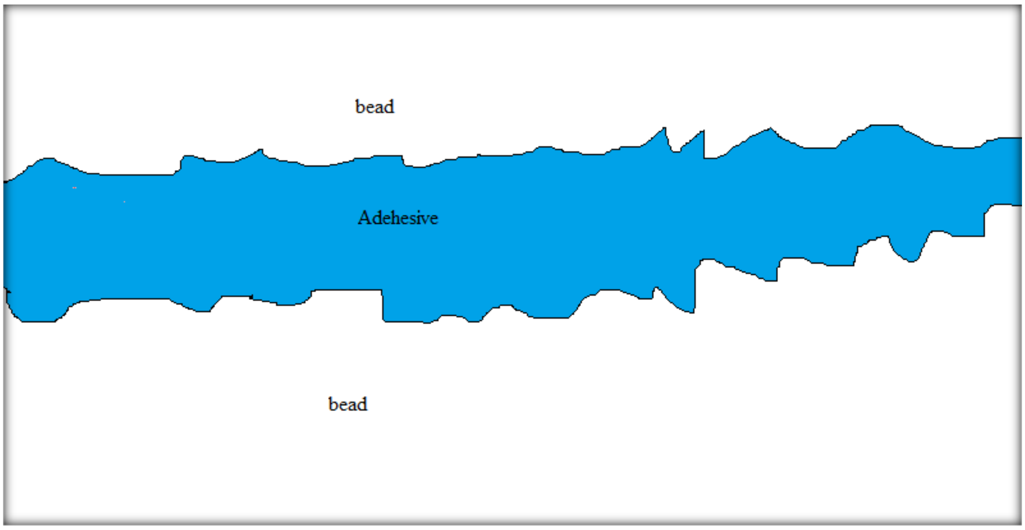


Figure 3.4: Interlocking concept (adhesion mechanism).

The highest effect found is that of the swelling time as revealed by the value of β_{12}, which is 27.04 g water/g hydrogel for a unit change of the coded time that is equivalent to 3 hours in actual time. This shows a direct effect of the time factor, which is quite expected. At the beginning of the experiment, the driving force for absorbing water is the osmotic pressure or the difference in water concentration inside and outside hydrogel. As the time goes on more water is absorbed by the hydrogel until reaching equilibrium, where the chemical potential of water inside and outside hydrogel becomes equal.

Regarding the effect of the solution pH (variable $C=X_3$) on the hydrogel absorption capacity, Eq. 6, shows that increasing the scaled pH by one unit (i.e., 1.5 on the real pH scale) in the range of 7 to 10 reduces the absorbency of hydrogel by only 2.8 g water/g hydrogel. Compared to the rest of main effects, the effect of pH was the least. The reduction of the hydrogel absorbency with increasing pH is believed to be a result of the interaction of carboxylate ions, which are attached to the backbone of poly acrylic acid hydrogels, with sodium ions. At higher levels of pH, more sodium hydroxide is applied to regulate the level of pH which raises the concentration of sodium ions in the solution, which in turn means more Na^+ ions inside hydrogel to balance its concentration outside hydrogel. Therefore, raising the concentration of sodium ions in solution increases its uptake by hydrogel. These ions are attracted to the carboxylate ions inside hydrogels because of the electrostatic interaction between them.

Sodium ions neutralize the carboxylate groups and eliminate the anion-anion repulsion between them. This repulsion enhances the absorbency by increasing the available spaces between hydrogel`s strands to store water. Therefore, eliminating the repulsion reduces absorbency [42].

Finally, regarding main effects, the effect of temperature is considered. Temperature is found to be a key factor that affects the absorbency of poly acrylic acid hydrogels. This is apparent from the high value of β_4 as shown in Eq. 6 coefficient. Increasing the temperature from 31.5 to 40^{o}C (one coded unit) enhances the absorbency of commercial hydrogels by 14.72 g water/g hydrogel. It is known that the main force stands behind the absorbency of hydrogels is the osmotic pressure [21]. The water molecules tend to move to the side of high osmotic pressure which is the phase of hydrogel at the beginning of the experiment. The hydrogel absorbs water until equilibrium or saturation is reached. Higher temperature accelerates the diffusion of water molecules inside hydrogel. Moreover, high temperature enhances the mobility of hydrogel`s chains which facilitates the expansion of networks with the absorption of water. Therefore, the temperature increases the available space inside hydrogel for water which consequently enhances the saturation of hydrogel [43]. From Eq. 6, it can be recognized that the highest effect is for the swelling time by 27.04 g water/g hydrogel for each unit of time. The same effect can be obtained by decreasing the hydrogel amount and increasing temperature by a value of one unit for each. Applying lower amount of hydrogel at higher temperature can be recommended to decrease the time needed for.

In view of these results, and since most of hydrogel`s applications require high level of pH (>7) [40], applying small amount of hydrogel can be encouraged [40]. The negative effect of one unit increase in coded pH (i.e., 2.8 on a real pH scale) can be eliminated by decreasing the units of hydrogel amount by 0.26 unit.

3.2.2. Multiple interaction effects. One important feature of full factorial design is the ability to study not only the main effects of input variables, but also the effects of all possible interactions between these variable on the response variable(s). For a 2^4 full factorial design there are binary (AB, AC, AD, BC, BD, and CD) interactions, ternary (ABC, ABD, BCD) interactions and quaternary (ABCD) interactions. This section addresses the effect of these different interactions between the input parameters.

It is interesting to observe that, except for the BD (temperature-contact time) binary effect, all binary interaction effects are negative meaning that at the higher level of variables (except the BD effect) the response variable (water absorption capacity) decreases. This is clearly observed in Figure 3.5 which represents a bar chart for all binary interactions involved. It is also clear from this figure (and also from the different values of β_{ij} in Eq. 6) that the x_{12} (amount of hydrogel-time interaction) and x_{14} (amount of hydrogel-temperature) are having the highest interaction. For example, at the higher level of the amount of hydrogel and the contact time, the absorption capacity of the hydrogel decreases 4.5 g water/g hydrogel. However, it can be noticed that the negative effect of increasing time and hydrogel amount is less than the single effect of hydrogel amount. This means that the negative effect of the amount of hydrogel decreases by time. As the swelling progresses, the beads expand with the absorption of water. When beads expand, the volume of voids (roughness) on their surfaces reduce which consequently decreases the bonding between beads. Therefore, the reduction in water uptake due to the bonding between beads reduces. Figure 3.6 (a) shows the interaction effect of hydrogel amount (factor A) and swelling time (factor B). From the figure, the improvement of absorption with time at low level of hydrogel amount is higher for the lower effect of bonding.

The interaction effect of swelling time (factor B) with pH (factor C) is shown in Figure 3.6 (b). It is clear that this is a weak negative effect; the absorption capacity of the hydrogel is reduced by 2.6 g water/g hydrogel when both factors are at their high level. This can be explained by the effect of time on the attached carboxylate ions inside hydrogel. As absorption progresses, the concentration of sodium ions inside the hydrogel increases to balance their concentration outside hydrogel. Sodium ions shield the negative charge inside hydrogels and prevent the repulsion between them. Therefore, the swelling of hydrogel decreases with time at high concentration of sodium ions in solution. Figure 3.6 (b) illustrates the effect of time on absorbency at the two levels of the pH factor. At the beginning of each experimental run, the difference between absorbencies at the high and low level of pH is small but as time goes on to the higher level the difference in absorbency increases to about 10.8 g water/g hydrogel as compared to 5.22 g water/g hydrogel at the low levels of pH and time, as shown by Figure 3.6 (b). This effect is mainly due to the interaction between time and pH, where absorbency is improved more at low level of pH.

The temperature-contact time effect is the only binary effect that is positive. At the higher levels of both factors the absorbency increased by 5.02 g water/g hydrogel. Within the temperature range studied here, the temperature enhances the hydrogel saturation uptake capacity of water which needs time to be reached. Moreover, the temperature speeds up the diffusion of solution inside hydrogel. Figure 3.6 (c) shows the positive effect of increasing temperature along with time. This is can be noticed from the slope of the two lines of absorbency at high and low levels of temperature.

On other hand, the temperature has negative effect if it is increased at high level of pH. The temperature does not accelerate only the diffusion of water molecules but also the diffusion of sodium ions. The increase of sodium ions inside hydrogel decreases its absorbency as explained before. Figure 3.6 (d) describes the interaction effect of temperature and pH. From this figure, it can be observed that the positive effect of temperature on absorbency decreases as the pH increases.

Figure 3.6 (e) shows how the interaction effect of temperature and hydrogel amount. Increasing the temperature along with hydrogel amount reduces the absorbency by 3.88 g water/g hydrogel. However, this negative effect of the interaction is less than the single effect of hydrogel amount; this can be explained in terms of the effect of temperature in enhancing the saturation uptake capacity of the hydrogel and the resulting improvement in mass transfer.

The high levels of pH and hydrogel amount reduces the absorbency by 2.5 g water/g hydrogel as evident in Figure 3.6 (f). This absorbency is due to the effect of pH on the concentration of sodium ions inside hydrogels and the effect of hydrogel amount on bonding between beads. However, the interaction effect of pH and hydrogel amount is the lowest in comparison to the single effects of pH and hydrogel amount. This can be explained as follows: Increasing the amount of hydrogel material reduces the effectiveness of each bead because of the higher number of surrounding beads that can bond with the bead and hence block its absorbency. The effect of bonding between beads, which does not only decrease the water uptake but also the absorbency of sodium ions as well, reduces the effect of increased pH on absorbency. Furthermore, this improvement on absorbency, due to the reduction of sodium ion concentrations inside hydrogel, expands beads and reduces the roughness of their surfaces. This reduction in roughness decreases the bonding between beads and enhances absorbency.

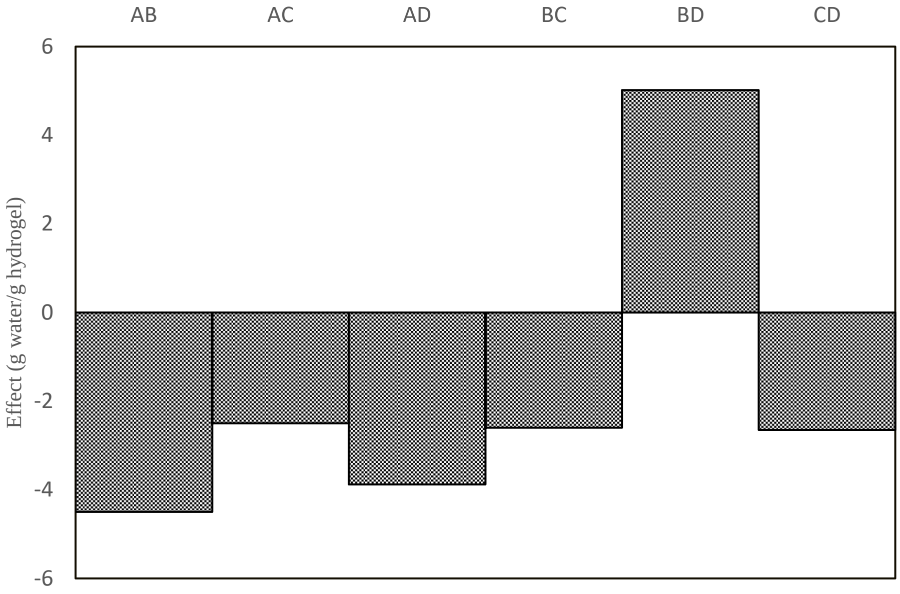


Figure 3.5: Binary Interaction effects of environmental parameters.

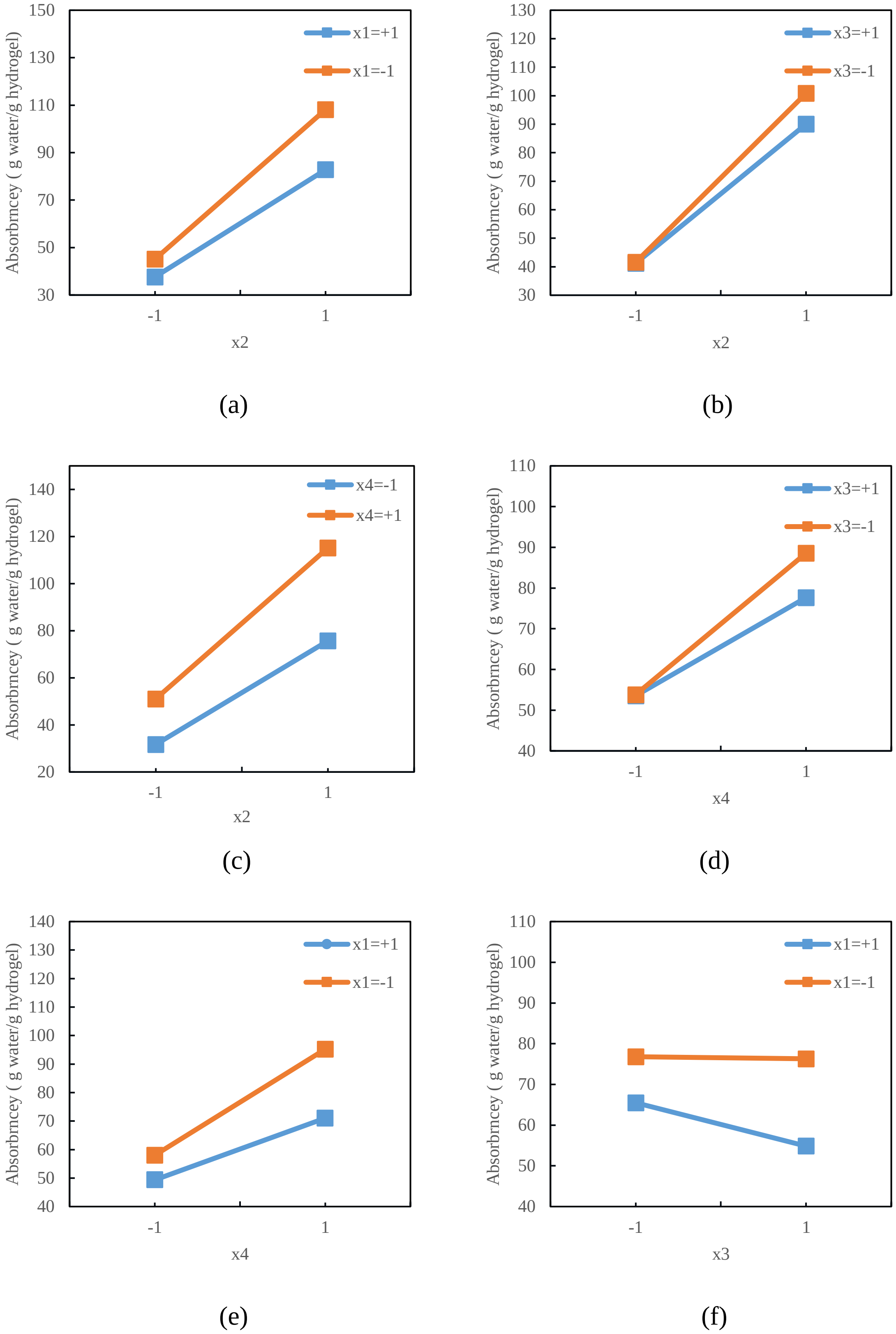


Figure 3.6: Interaction effects of parameters: (a) hydrogel amount-swelling time, (b) pH-swelling time, (c) temperature-swelling time, (d) pH-temperature, (e) hydrogel amount-temperature, (f) hydrogel amount-pH.

It is clear that, except for the ACD interaction, all ternary interaction effects have adverse effect on absorbency which can be observed through Figure 3.7. However, a positive effect of 4.7 g water/g hydrogel can be noticed for the quaternary interaction effect, ABCD, as shown by Figure 3.7.

Based on the experimental results obtained and the effects of parameters studied in this work, the best absorbency that can be obtained from this type of beads over in the ranges of parameters taken here is 147.3 g water/g hydrogel, which is obtained using 0.12 g of hydrogel, 8 hours for the swelling time, pH of 7, and a temperature of 40°C. On other hand, the lowest absorbency (29.1 g water/g hydrogel) has been obtained using the high levels of hydrogel amount and pH at the low levels of temperature and swelling time. These conditions of the lowest and highest absorbencies can be used to summarize the effects of environmental parameters.

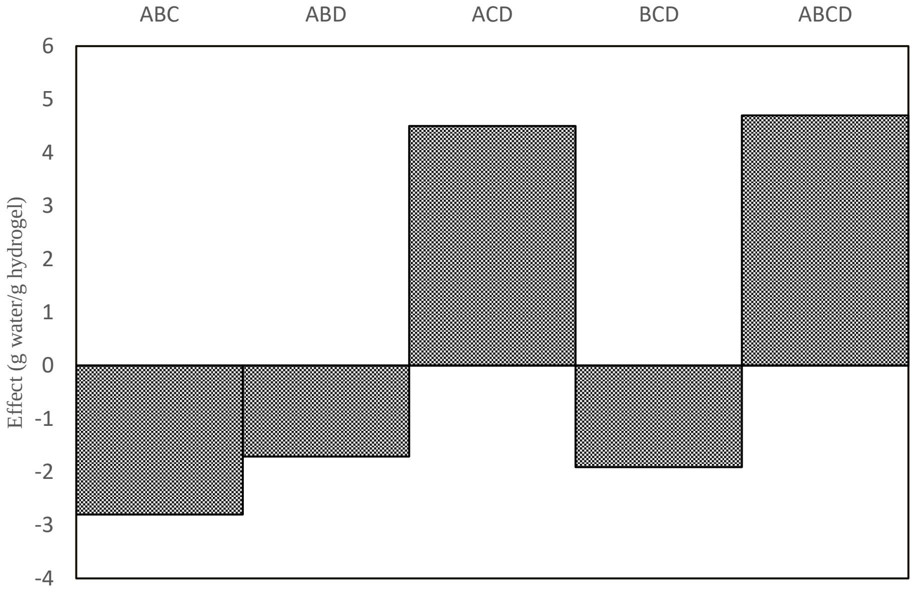


Figure 3.7: Ternary and quaternary interaction effects of environmental parameters.

3.2.3. Model adequacy. Figure 3.8 shows the normal probability plot of residuals. As can be concluded from comparing the residuals plot with the ideal normal distribution plot represented by the best-fit straight line, the general conclusion that can be inferred from this figure is that the distribution of residuals is approximately normal.

The tendency of normal plot to bend slightly upwards on the left side and downwards on the right side, indicates that the tails of residuals distribution are thinner, in term of located data, than what is anticipated by the normal distribution. Moreover, the symmetricity of residuals around their median can be clearly recognized in Figure 3.9. The standardized residuals have been calculated, using Eq. (4), and presented in Table 3.4. As shown in this table, all standardized residuals are in the range of -1 to +1.

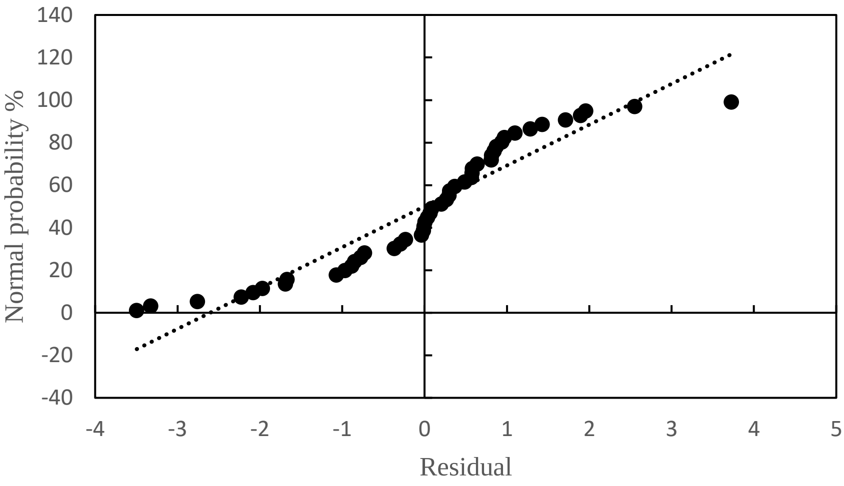


Figure 3.8: Normal probability plot for residuals of absorbency for commercial hydrogels.

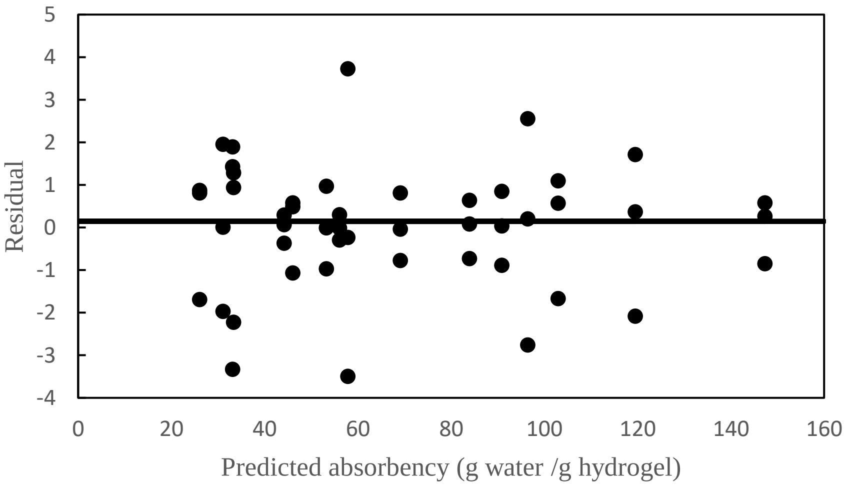


Figure 3.9: Residuals of absorbency for commercial hydrogels.

Table 3.4: Residuals and standardized residuals of predicted absorbencies.

Run	Absorbency (g water/g hydrogel)	Predicted Absorbency (g water/g hydrogel)	Residuals	Standardized Residuals
1	29.83	33.15	-3.33	-0.11
	34.58		1.43	0.05
	35.05		1.90	0.06
2	29.88	29.07	0.81	0.03
	27.38		-1.69	-0.06
	29.94		0.87	0.03
3	69.92	69.11	0.81	0.03
	68.34		-0.78	-0.03
	69.08		-0.03	0.00
4	83.24	83.97	-0.73	-0.02
	84.61		0.64	0.02
	84.05		0.09	0.00
5	31.10	33.33	-2.23	-0.07
	34.27		0.94	0.03
	34.62		1.28	0.04
6	33.04	31.08	1.96	0.06
	29.12		-1.97	-0.06
	31.09		0.01	0.00
7	93.69	96.45	-2.76	-0.09
	99.01		2.55	0.08
	96.66		0.20	0.01
8	54.25	53.28	0.97	0.03
	52.32		-0.97	-0.03
	53.28		0.00	0.00
9	61.62	57.90	3.72	0.12
	57.67		-0.23	-0.01
	54.40		-3.49	-0.12
10	45.01	46.08	-1.07	-0.04
	46.66		0.58	0.02
	46.57		0.49	0.02
11	147.91	147.33	0.58	0.02
	147.59		0.27	0.01
	146.48		-0.85	-0.03
12	101.28	102.95	-1.67	-0.06
	103.52		0.57	0.02
	104.05		1.10	0.04
13	56.06	56.07	-0.01	0.00
	56.37		0.30	0.01
	55.77		-0.29	-0.01
14	44.25	44.18	0.07	0.00
	44.47		0.30	0.01
	43.81		-0.37	-0.01
15	121.23	119.52	1.71	0.06
	119.88		0.37	0.01
	117.44		-2.08	-0.07
16	90.00	90.89	-0.88	-0.03
	90.93		0.04	0.00
	91.73		0.85	0.03

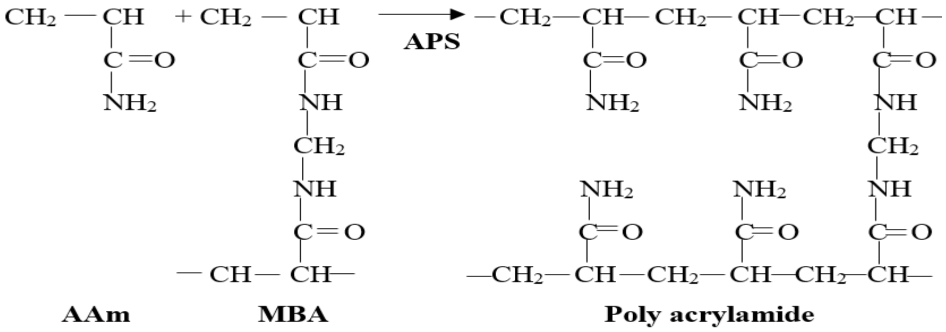
Chapter 4. Results and Discussion: Synthetic Poly Acrylamide Hydrogels

In this chapter, the synthesis of poly acrylamide hydrogels is described and the effects of synthesis parameters on its water uptake capacity are examined. The two-level factorial design methodology has been used to design experiments and develop a regression model for the absorbency of the synthesized poly acrylamide hydrogels. The coefficients of this model are used to discuss the main and interaction effects of the synthesis parameters on the hydrogel water-absorption capacity. Furthermore, the model adequacy is checked and the experimental FTIR results of all prepared poly acrylamide hydrogels are discussed.

4.1. Methodology

4.1.1. Synthesis of poly acrylamide hydrogels. Acrylamide (AAm) was supplied by SDFCL Sd fine-chem limited with a purity of 98.5%, N, N'-methylene-bisacrylamide (MBA and N,N,N',N'- tetramethylethylenediamine (TEMED) were obtained from Sigma-Aldrich with stated purities of 99%, and Ammonium persulfate (APS) was purchased from Merck with a stated purity of 98%. All materials were used as received with no further purification.

The free-radical polymerization method was used to synthesize the polymeric hydrogel used in this work. The acrylamide was dissolved in 30 ml of distilled water followed by the addition of the cross-linker MBA. Nitrogen gas was bubbled through the solution for 10 minutes to remove any dissolved oxygen gas that can inhibit the polymerization process. APS was added to the solution in the presence of the accelerator TEMED. The APS as a 10% (w/w) solution with an equal amount of TEMED, was added to the mixture as suggested by Rodrigues et al. [44]. The polymerization reaction of acrylamide proceeds as indicated by the following overall chemical reaction:



Two hours after addition of the initiator and the accelerator the mixture was casted into manually prepared PVC molds immediately at room temperature. PVC straws with diameter of 3 mm were cut into cylinder/ical shapes of 4-5 mm in length, and used as a casting mold of the synthesized gel as shown in Figure 4.1. The gel was dried for 2 days at 50^{o}C in a dryer (GENLAB,UK) Produced gel was allowed to reach its maximum absorbency at room temperature using distilled water.

Figure 4.1: Casting mold of hydrogel on straws.

4.1.2. Two-level experimental factorial design. Two-level factorial design was employed to study the effects of monomer, cross-linker, and initiator concentrations on the synthesized poly acrylamide hydrogels. Table 4.1 shows the levels and symbols of factors in the factorial design. The percentages of monomer are based on mass relative to water and those of the crosslinker and the initiator are based on moles relative to moles of monomer. The Eight samples of poly acrylamide hydrogel have been prepared considering all the possible combinations of factors. Each run was repeated three times, to find experimental error, and the average was taken for their absorbencies.

Table 4.2 summarizes the results of the conducted runs, together with the resulting main (single), and multiple interaction effects. The effects have been found in the form of a regression model as given by Eq. 7.

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{12} x_1x_2 + \beta_{13} x_1x_3 + \beta_{23} x_2x_3 + \beta_{123} x_1x_2x_3 \quad (7)$$

Where: y is the predicted absorbency, the betas are the main and interaction effects parameters, and x_1, x_2, and x_3 represent the values of coded (scaled) input factors. The relation between natural and coded variables are given by Eq. 8. The betas are obtained by taking the average of absorbencies after multiplying them by the signs of related factors [38].

$$x_1 = \frac{Xi - \frac{Xi,_{high} + Xi,_{low}}{2}}{\frac{Xi,_{high} - Xi,_{low}}{2}} \quad (8)$$

Where $X_{i,high}$ and $X_{i,low}$ indicates the high and low levels of input parameter, i.e. monomer concentration (A), cross-linker concentration (B), and initiator concentration (C), and x_i is the corresponding coded variable (i.e., ranged between -1 and +1).

Table 4.1: Symbols, high, and low levels of synthetic factors in factorial design.

Factor	Symbol	Low Level	High Level
Monomer concentration	A	7 %	17%
Cross-linker concentration	B	0.5%	3%
Initiator concentration	C	0.1%	0.5%

Table 4.2: Factorial design matrix for input parameters (synthetic parameters).

Run	A	B	C	AB	AC	BC	ABC
1	-1	-1	-1	1	1	1	-1
2	1	-1	-1	-1	-1	1	1
3	-1	1	-1	-1	1	-1	1
4	1	1	-1	1	-1	-1	-1
5	-1	-1	1	1	-1	-1	1
6	1	-1	1	-1	1	-1	-1
7	-1	1	1	-1	-1	1	-1
8	1	1	1	1	1	1	1

The residuals and the corresponding normal probability plots were employed to check for the adequacy of obtained regression model.

4.2. Results and Discussion

Table 4.3 summarizes the amounts of acrylamide, MBA, and APS that have been applied, as well as the obtained absorbencies in all conducted runs. The values of main and interaction coefficients were calculated and reported as in Eq. 9.

$$y = 10.5 - 2.51\ x_1 - 3.01\ x_2 + 0.98\ x_3 + 0.2\ x_1x_2 - 0.42\ x_1x_3 - 0.3\ x_2x_3 - 0.173\ x_1x_2x_3 \qquad (9)$$

Table 4.3: Absorbencies of poly acrylamide hydrogels in all conducted runs.

Run	**Factorial combinations**			**AAm (g)**	**MBA (g)**	**APS (μL)**	**Absorbency (g water/g hydrogel)**	**Average of Absorbency (g water/g hydrogel)**
	A	**B**	**C**					
1	-1	-1	-1	2.11	0.02	68.00	14.05	14.66
				2.11	0.02	68.00	15.43	
				2.11	0.02	68.00	14.49	
2	1	-1	-1	5.11	0.06	164.00	10.42	9.81
				5.10	0.06	164.00	9.56	
				5.11	0.06	164.00	9.45	
3	-1	1	-1	2.10	0.14	68.00	9.27	8.51
				2.10	0.14	68.00	7.88	
				2.10	0.14	68.00	8.39	
4	1	1	-1	5.10	0.33	164.00	5.07	5.03
				5.10	0.34	164.00	5.09	
				5.11	0.34	164.00	4.95	
5	-1	-1	1	2.11	0.02	339.00	18.19	17.67
				2.10	0.02	339.00	17.36	
				2.11	0.02	339.00	17.47	
6	1	-1	1	5.10	0.06	823.00	12.53	11.82
				5.11	0.06	823.00	11.30	
				5.11	0.06	823.00	11.63	
7	-1	1	1	2.11	0.14	339.00	11.77	11.09
				2.10	0.14	339.00	10.76	
				2.10	0.14	339.00	10.75	
8	1	1	1	5.10	0.33	823.00	5.56	5.23
				5.10	0.34	823.00	4.88	
				5.10	0.34	823.00	5.25	

4.2.1. Main effects of input variables. Figure 4.3 shows the main effects of input variables which can be described by the coefficients β_1, β_2, and β_3. The main effect of monomer concentration is given by the coefficient β_1, which is -2.51 g water/g hydrogel. The negative sign of this coefficient denotes a negative influence of monomer concentration on the water capacity of the synthesized poly acrylamide hydrogels. This can be referred to the effect of increasing monomer concentration on the density of chains inside the resulting polymer networks. At high level of monomer concentration dense networks are formed, which have low water capacity as discussed elsewhere [37]. Furthermore, the water inside poly acrylamide hydrogel can exist in the form of polarized or free water as depicted in Figure 4.2. The polarized molecules are attracted to the hydrophilic groups (-$CONH_2$) while the free water is imbedded in the capillary pores. The amount of polarized water in hydrogel depends on the number of hydrophilic groups which increases as the monomers in chains increases. On other hand, the concentration of free water in hydrogel increases as the volume of free spaces in network increases. At the beginning of their contact with the hydrogel, the water molecules penetrate through the hydrogel because of attraction to the hydrophilic groups and because of the effect of osmotic pressure. Therefore, as the number of monomers in chains increases, the absorbency enhances for the higher density of hydrophilic group. However, as the swelling progresses, the polymer is diluted by water and the chains move further which decreases the effect of hydrophilic groups. Thereafter, any absorbed water by hydrogel will be due to the osmotic pressure. The absorbency of water pursues until the filling of the available spaces between chains (saturation). The saturation state is minimized by decreasing the available spaces between chains (increasing the density of chains) which depends on applied monomers. Therefore, using higher concentration of monomer decreases absorbency by reducing the available spaces for free water [45].

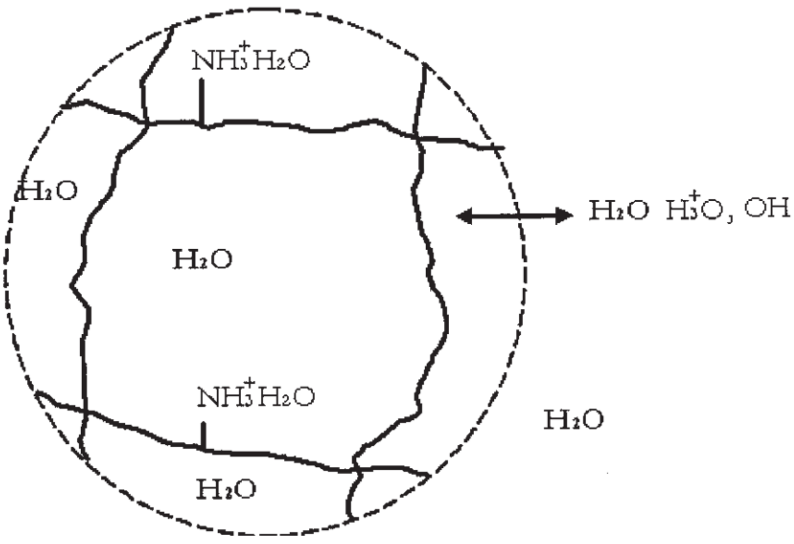


Figure 4.2: Different water formation inside poly acrylamide hydrogel [45].

The cross-linker concentration has the highest effect in comparison with the other main effects of monomer and initiator concentrations. Raising the scaled cross-linker concentration by one unit, which is equivalent to 1.25 % on the real scale, decreases the absorbency of poly acrylamide hydrogels by 3.01 g water/g hydrogel. The function of cross-linkers is to link between the chains of polymer to form a gel. However, increasing the concentration of cross-linker enhances the bonds between chains which decreases the opportunity of water to penetrate the spaces between chains [30].

Increasing the initiator concentration by one unit on the coded scale, i.e., 0.2% on the real scale, improves the absorbency of hydrogel by 0.98 g water/g hydrogel. The effect of initiators can be explained using Flory theory as discussed by Singhal et.al [30]. The relationship between the swelling ratio and network structure parameters has been developed by Flory for charged networks as follows [30]:

$$p_m^{5/3} \approx \ [(\frac{i}{2\upsilon_u} \times \frac{1}{S^{1/2}})^2 + ((1/2 + \chi_1)\upsilon_1)]\ ^2 \times (\frac{M_c}{\rho_p}) \times (1 - \frac{2M_c}{M_n})^{-1} \qquad (10)$$

Where:

p_m is swelling ratio

$\frac{i}{2\upsilon_u}$ is the concentration of fixed charge in network.

S is the ionic strength of the swollen solution.

$\chi_1$is the polymer– solvent thermodynamic interaction parameter.

M_c is the average molecular weight of polymer between cross-links.

ρ_p is the density of polymer.

$M_n$is the average molecular weight of polymer in network chains.

The high concentration of initiators increases the chain ends in networks since it raises the number of radical monomers, and the average molecular weight of polymer in network (M_n) decreases as the number of chain ends enhances, as reported elsewhere [30]. From Flory relation, it is predicted that the networks with lower molecular weight (higher chain ends) have higher swelling ratio [30].

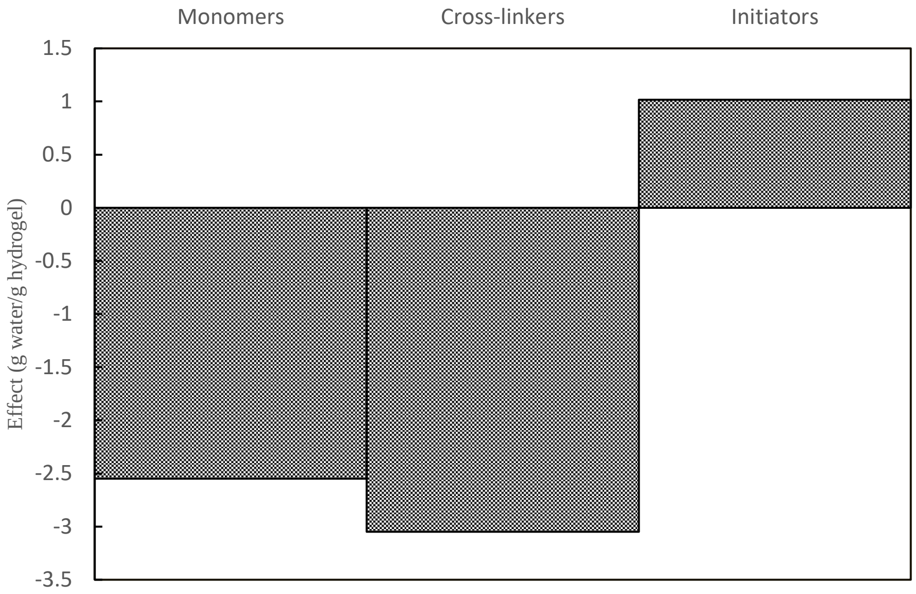


Figure 4.3: Main effects of monomer, cross-linker and initiator concentrations.

4.2.2. Multiple interaction effects. For a 2^3 full factorial design, there are three binary interactions (AB, AC, and BC) and one ternary interaction (ABC). Figure 4.4 is a bar chart that describes all the interaction effects. It can be noticed that all the interaction effects have negative influence on water capacity except the AB (monomer and cross-linker concentrations) interaction which enhances absorbency. This positive effect of monomer concentration along cross-linker concentration can be explained as follows: Raising monomer concentration increases the density of networks which necessitates more cross-linkers to join between them. On other hand, improving the cross-linkers by one coded unit does not seem enough to satisfy this increase in demand. Therefore, by applying high level of monomer concentration the strength of bonding between chains decreases, and the ability of water to penetrate the spaces between chains enhances. Figure 4.5 (a) illustrates the effect of increasing cross-linker concentration on absorbency at high and low level of monomer concentrations. It is observed from this figure that increasing cross-linker concentration reduces the absorbency of hydrogel, along high or low concentration of monomer, because of its effect on enhancing bonding between chains. However, the effect of cross-linkers decreases as the concentration of monomers increases for the positive effect of their interaction.

The effect of initiator -monomer interaction and initiator-cross liker interaction decreases absorbency of poly acrylamide hydrogel by 0.42 and 0.3 g water/g hydrogel, respectively, as illustrated by Figure 4.5 (b) and (c). The initiators reduce the molecular weight of polymer in chains which has positive effect on water uptake as explained before using Flory relation. However, this positive influence of initiators is not enough to balance the negative effects of monomers or cross-linkers, a thing that can also be used also to explain the negative effect of the ternary (ABC) interaction.

The swelling rate of hydrogels is an important factor in many applications (such as the industry of disposable diapers) [23]. This property for hydrogels depends mainly on the pores or the empty available spaces in hydrogels to hold water. As was presented in the literature review of this thesis, the porosity or the empty spaces in the structure of superabsorbent hydrogels can be increased by decreasing monomer or cross-linker concentrations, and increasing initiator concentration.

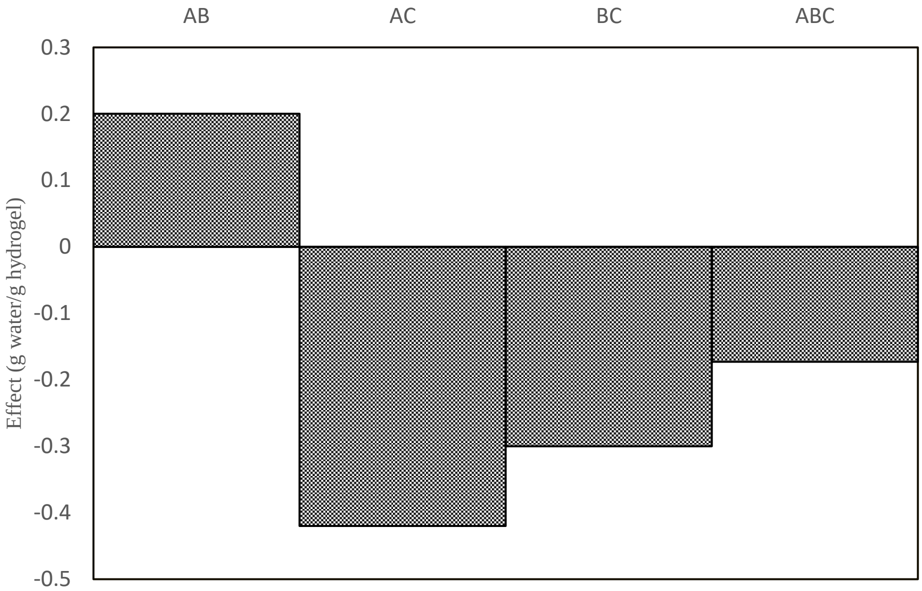
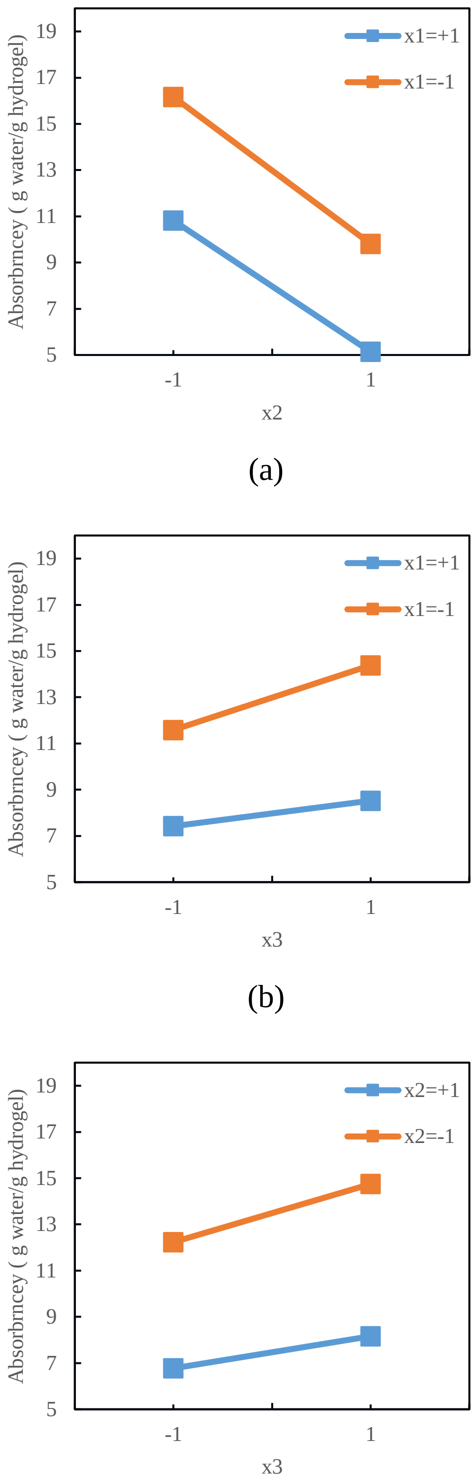


Figure 4.4: Binary and ternary interaction effects of synthetic parameters.



(a)

(b)

(c)

Figure 4.5: Interaction effects of the studied input factors: (a) monomer-cross-linker concentrations, (b) monomer-initiator concentrations, and (c) cross-linker-initiator concentrations.

4.2.3. Model adequacy. The normal probability plot of residuals is presented in Figure 4.6. Moreover, the predicted absorbencies have been plotted versus their residuals in Figure 4.7. The two plots appear satisfactory in term of normal probability and symmetricity around median. Furthermore, all the standardized residuals as calculated using Eq. 4 are in the range of -1 to +1 as shown by Table 3.4.

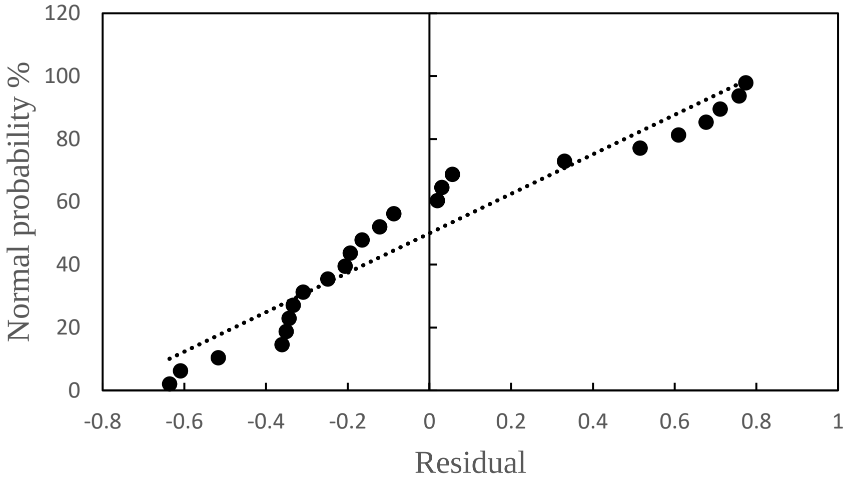


Figure 4.6: Normal probability plot of residuals for poly acrylamide hydrogels absorbencies.

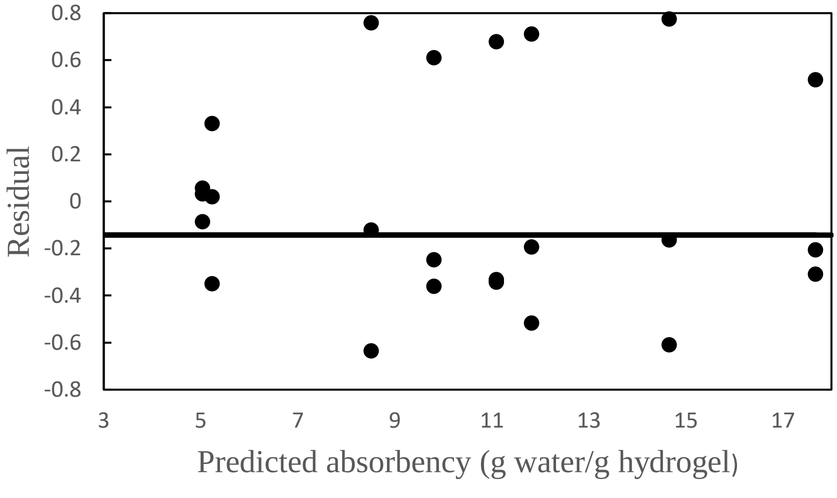


Figure 4.7: Residuals of absorbencies for poly acrylamide hydrogel.

Table 4.4: Residuals and standardized residuals of predicted absorbencies for poly acrylamide hydrogels.

Run	Absorbency (g water/g hydrogel)	Predicted Absorbency (g water/g hydrogel)	Residuals	Standardized Residuals
1	14.05	14.66	-0.61	0.00
	15.43		0.77	0.01
	14.49		-0.16	0.00
2	10.42	9.81	0.61	0.00
	9.56		-0.25	0.00
	9.45		-0.36	0.00
3	9.27	8.51	0.76	0.01
	7.88		-0.64	0.00
	8.39		-0.12	0.00
4	5.07	5.03	0.03	0.00
	5.09		0.06	0.00
	4.95		-0.09	0.00
5	18.19	17.67	0.52	0.00
	17.36		-0.31	0.00
	17.47		-0.21	0.00
6	12.53	11.82	0.71	0.00
	11.30		-0.52	0.00
	11.63		-0.19	0.00
7	11.77	11.09	0.68	0.00
	10.76		-0.33	0.00
	10.75		-0.34	0.00
8	5.56	5.23	0.33	0.00
	4.88		-0.35	0.00
	5.25		0.02	0.00

4.2.4. Fourier transform infrared (FTIR) spectroscopy. Figure 4.8 describes the FTIR spectrum for one sample of the prepared poly acrylamide hydrogel. Strong peaks can be recognized at 3423.07 cm^{-1} for the attribution of $-NH_2$, at 2917.58 cm^{-1} for the contribution of $-CH_2$, and at 1640.61 cm^{-1} for the stretching of -C=O [46, 47]. Approximately, the same peaks can be observed for the synthesized poly acrylamide hydrogels of other samples as shown by Figures A.1 to A.7.

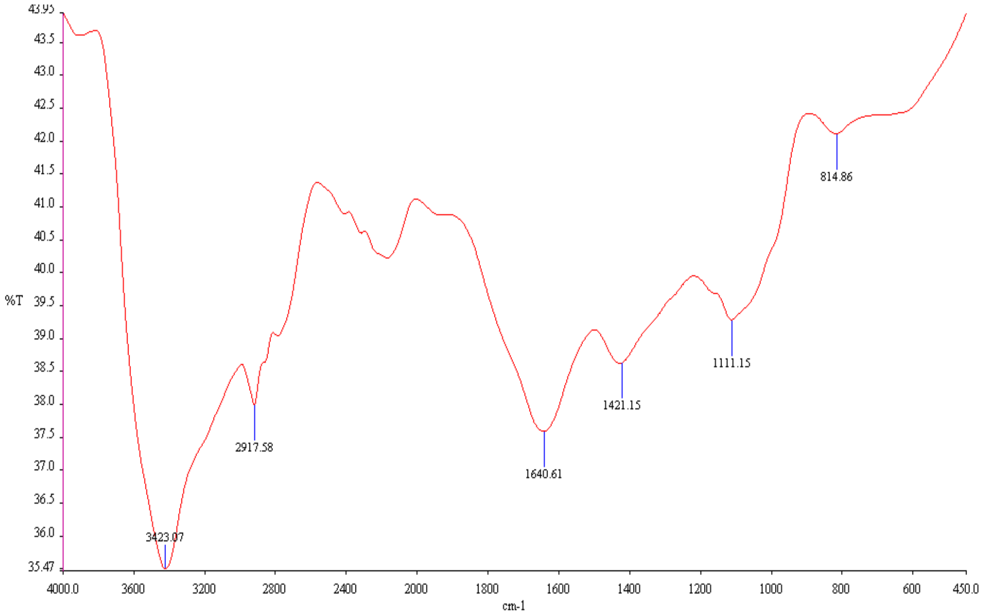


Figure 4.8: Sample FTIR results of the synthesized poly acrylamide hydrogel.

Chapter 5. Conclusions and Recommendations

In this study, a comprehensive literature survey covering the different classifications, synthesis methods, characteristics, water uptake capacity, and different uses and applications of polymeric hydrogel materials was conducted. In particular, water uptake capacity of polymeric hydrogel materials was the point of emphasis in this study. The parameters that have effects on hydrogel water absorbency were screened and the effects of ionic strength, pH, and medium temperature, as well as the concentrations of monomers, cross-linkers, and initiators were reviewed as per the open technical literature. Most of the conducted studies in the literature investigated the main effects of these parameters without any examination for their interaction effects.

In this thesis, the effects of hydrogel amount, swelling time, pH, and medium temperature on water absorbency of commercial hydrogels were studied using full two-level (2^4) factorial design. Based on practical considerations, high and low levels of each of the input factors were selected and the (16) experimental runs were conducted (in triplicate) to measure water absorbency of one specific (based on acrylic acid) commercial hydrogels. The resulting 2^4 full factorial model was used in the analysis of the main (single) and multi-interaction effects of the different input factors. It was found that the specific absorbency (i.e., absorbency based on unit mass of the hydrogel) decreased with increasing the amount of hydrogel, probably because of its effect on prohibiting the free swelling of some beads due to their bonding with the other surrounded beads which increased with the hydrogel amount. On other hand, the swelling contact time directly affect water absorbency as expected. The negative effect of pH on the water uptake capacity of the hydrogel was attributed to the reduction of anion-anion repulsion inside the hydrogel for the neutralization of carboxylate groups with sodium ions. The temperature enhanced the absorbency, which has been explained in terms of its effect in enhancing mass transfer inside the hydrogel phase and facilitating the expansion of networks to hold larger amount of water. However, it was found that at the higher levels of the hydrogel amount along, swelling contact time, pH, and temperature the water uptake capacity of the hydrogel was reduced. However, the negative effect of higher level of hydrogel amount along with other factors were less than its main effect for the positive influences of the other factors. Moreover, applying the high level of contact time or temperature along with pH decreased the water uptake for their effects in increasing the concentration of Na^+ ions inside hydrogel. Finally, the adequacy of developed model was checked using the normal probability plot, and the FTIR result of the commercial hydrogels was presented and discussed.

In this work also, the effects of monomer, initiator, and cross-linker concentrations on water uptake capacity of an experimentally prepared poly acrylamide hydrogel were studied. A 2^3 full factorial design was used in this study. The poly acrylamide hydrogels were prepared by radical polymerization of acrylamide in the presence of N,N-methylenebisacrylamide as a crosslinker and ammonium persulfate as an initiator. The hydrogel was prepared using 2-level factorial runs in triplicate considering the eight possible combinations in a 2^3 factorial design. A relation between absorbency and monomer, cross-linker, and initiator concentrations was developed and used to study the main and the multi-interaction effects. Increasing the monomer concentration reduced the absorbency, probably because of its effect on enhancing the density of chains inside networks. A higher level of cross-linkers was found to have a negative effect on the synthesized hydrogel water absorbency. This is believed to be resulting from the increased bonding between the polymer chains. On other hand, the initiators improved water absorbency of the synthesized hydrogel since it decreased the average molecular weight of polymer. However, the high levels of initiator concentration along monomer or cross-linker concentrations reduced absorbency for their influences in networks structure. The interaction effect of monomers and cross-linkers concentrations on water absorbency was found to be positive, probably because of the effect of monomers in reducing the negative influence of cross-linkers. The model was checked and the FTIR results of poly acrylamide hydrogels were analysed.

As to a future recommended work, since the effects of pH and temperature are related to the chains and the structure of networks, they can be examined along with monomer, cross-linker, and initiator concentrations. Furthermore, more parameters such as particle porosity and particle size can be studied using the two- or higher-level factorial design.

References

[1] K. R. Kamath and K. Park, “Biodegradable hydrogels in drug delivery,” *Adv. Drug Deliv. Rev.*, vol. 11, no. 1–2, pp. 59–84, 1993.

[2] R. Zarzycki, Z. Modrzejewska, K. Nawrotek, and U. Lek, “Drug Release From Hydrogel Matrices,” *Ecol. Chem. Eng. S*, vol. 17, no. 2, pp. 117–136, 2010.

[3] W. E. Hennink and C. F. van Nostrum, “Novel crosslinking methods to design hydrogels,” *Adv. Drug Deliv. Rev.*, vol. 64, no. SUPPL., pp. 223–236, 2012.

[4] S. Chirani,N., Yahia,L., Gritsch,L., Motta,F.,L., Chirani,S., Fare, “History and Applications of Hydrogels,” *J. Biomed. Sci.*, vol. 4, no. 2, pp/. 13, 2015.

[5] R. Singhal and K. Gupta, “A Review : Tailor-made Hydrogel Structures (Classifications and Synthesis Parameters),” vol. 2559, no. February 2017, 2016.

[6] E. M. Ahmed, “Hydrogel: Preparation, characterization, and applications: A review,” *J. Adv. Res.*, vol. 6, no. 2, pp. 105–121, 2015.

[7] F. Rodriguez, C. Cohen, C. K. Ober, and L. Archer, *Principles of Polymer Systems, Sixth Edition*. 2014.

[8] M. J. Zohuriaan-Mehr and K. Kabiri, “Superabsorbent Polymer Materials: A Review,” *Iran. Polym. J.*, vol. 17, no. 6, pp. 451–477, 2008.

[9] P. Weiss, A. Fatimi, J. Guicheux, and C. Vinatier, “Biomedical Applications of Hydrogels Handbook,” *Business*, vol. c, pp. 247–268, 2010.

[10] K. Gloria Huerta-Angeles, A. Hishchalk, B. Strachota, M. Strachota, and L. M. Slouf, “Super-porous nanocomposite PNIPAm hydrogels reinforced with titania nanoparticles, displaying a very fast temperature response as well as pH-sensitivity,” *Eur. Polym. J.*, vol. 59, pp. 341–352, 2014.

[11] K. Ramteke, “Stimuli Sensitive Hydrogels in Drug Delivery Systems.,” *Int. J. …*, vol. 3, no. 12, pp. 4604–4616, 2012.

[12] Y. Qiu and K. Park, “Environment-sensitive hydrogels for drug delivery,” *Adv. Drug Deliv. Rev.*, vol. 64, no. SUPPL., pp. 49–60, 2012.

[13] T. Mittal and S. Singh, “Potential Applicabilities of Hydrogels - A Literature Survey,” vol. 1, no. 3, pp. 1–15, 2012.

[14] M. A. Ward and T. K. Georgiou, “Thermoresponsive polymers for biomedical applications,” *Polymers (Basel).*, vol. 3, no. 3, pp. 1215–1242, 2011.

[15] H. Almeida, M. H. Amaral, and P. Lobão, “Temperature and pH stimuli-responsive polymers and their applications in controlled and selfregulated drug delivery,” *J. Appl. Pharm. Sci.*, vol. 2, no. 6, pp. 01–10, 2012.

[16] K. S. De, N. R. Aluru, B. Johnson, W. C. Crone, D. J. Beebe, and J. Moore, “Equilibrium swelling and kinetics of pH-responsive hydrogels: Models, experiments, and simulations,” *J. Microelectromechanical Syst.*, vol. 11, no. 5, pp. 544–555, 2002.

[17] J. Maitra and V. K. Shukla, "Cross-linking in Hydrogels - A Review," *Am. J. Polym. Sci.*, vol. 4, no. 2, pp. 25–31, 2014.

[18] F. L. Buchholz and A. T. Graham, *Modern Superabsorbent Polymer Technology*. Wiley-VCH, 1998.

[19] M. Bahram and N. Mohseni, "An Introduction to Hydrogels and Some Recent Applications." *Emerging Concepts in Analysis and Applications of Hydrogels*, vol. 2, pp. 9–38, 2016.

[20] Y. Cai *et al.*, "Towards temperature driven forward osmosis desalination using Semi-IPN hydrogels as reversible draw agents," *Water Res.*, vol. 47, no. 11, pp. 3773–3781, 2013.

[21] J. Höpfner, *Seawater Desalination Via Acrylic Acid Based Hydrogels*. KIT Scientific, 2013.

[22] M. J. Zohuriaan-Mehr, H. Omidian, S. Doroudiani, and K. Kabiri, "Advances in non-hygienic applications of superabsorbent hydrogel materials," *J. Mater. Sci.*, vol. 45, no. 21, pp. 5711–5735, 2010.

[23] R. Ahmed and K. A. Syed, "Synthesis of Superabsorbent Polymer (SAP) via Industrially Preferred Route," *Lifescience global*, vol. 12, pp. 383–387, 2016.

[24] E. Caló and V. V. Khutoryanskiy, "Biomedical applications of hydrogels: A review of patents and commercial products," *Eur. Polym. J.*, vol. 65, pp. 252–267, 2015.

[25] D. Jhurry, "Agricultural Polymers," *Food Agric. Res. Counc. Réduit*, pp. 109–113, 1997.

[26] J. Byun, "Electro-Responsive Hydrogels for a Facile Desalination," vol. 101, no. 26, pp. 5093, 2011.

[27] P. B. L. Fregolente, M. R. Wolf Maciel, and L. S. Oliveira, "Removal of water content from biodiesel and diesel fuel using hydrogel adsorbents," *Brazilian J. Chem. Eng.*, vol. 32, no. 4, pp. 895–901, 2015.

[28] J. Alaei, S. H. Boroojerdi, and Z. Rabiei, "Application of Hydrogels in Drying Operation," *Petroluem & Coal*, vol. 47, pp. 32–37, 2005.

[29] D. Buenger, F. Topuz, and J. Groll, "Hydrogels in sensing applications," *Prog. Polym. Sci.*, vol. 37, no. 12, pp. 1678–1719, 2012.

[30] R. Singhal, R. S. Tomar, and A. K. Nagpal, "Effect of cross-linker and initiator concentration on the swelling behaviour and network parameters of superabsorbent hydrogels based on acrylamide and acrylic acid," *Int J Plast Technol*, vol. 13, no. 1, pp. 22–37, 2009.

[31] F. Habeeb Jabrail and M. E. Mahmood, "Hydrophilic Monomers Graft Gum Arabic Hydrogels Prepared in Different Cross-linking Nature and Study of their Effects on Irrigation of Agriculture Soil," *Res. J. Chem. Sci*, vol. 6, no. 1, pp. 2231–606, 2016.

[32] D. Li, X. Zhang, G. P. Simon, and H. Wang, "Forward osmosis desalination

using polymer hydrogels as a draw agent: Influence of draw agent, feed solution and membrane on process performance," *Water Res.*, vol. 47, no. 1, pp. 209–215, 2013.

[33] G. R. Mahdavinia, S. B. Mousavi, F. Karimi, G. B. Marandi, H. Garabaghi, and S. Shahabvand, "Synthesis of porous poly(acrylamide) hydrogels using alcium carbonate and its application for slow release of potassium nitrate," *Express Polym. Lett.*, vol. 3, no. 5, pp. 279–285, 2009.

[34] Z. Jiang, X. Cao, and L. Guo, "Synthesis and swelling behavior of poly (acrylic acid-acryl amide-2-acrylamido-2-methyl-propansulfonic acid) superabsorbent copolymer," *J. Pet. Explor. Prod. Technol.*, vol. 7, no. 1, pp. 69–75, 2017.

[35] I. A. & A. M. L. LIM SZE LIM, "pH Sensitive Hydrogel Based on Poly (Acrylic Acid) and Cellulose Nanocrystals," *Sains Malaysiana*, vol. 44, no. 6, pp. 779–785, 2015.

[36] P. Ass, M. A. Mutar, and R. K. Kmal, "Preparation of copolymer of acrylamide and acrylic acid and its application for slow release sodium nitrate fertilizer," *J. Al-Qadisiyah Pure Sci.*, vol. 17, no. 4, pp. 1–23, 2012.

[37] R. S. Tomar, I. Gupta, R. Singhal, and A. K. Nagpal, "Synthesis of poly (acrylamide-co-acrylic acid) - based super-absorbent hydrogels by gamma radiation : study of swelling behaviour and network parameters," *Des. Monomers Polym.*, vol. 10, no. 1, pp. 49–66, 2007.

[38] D. C. Montgomery, *Design and Analysis of Experiments Eighth Edition*. John Wiley & Sons, 1984.

[39] B. MAQ and M. S. Rahman, "Improvement of Swelling Behaviour of Poly (Vinyl Pyrrolidone) and Acrylic Acid Blend Hydrogel Prepared By the Application of Gamma Radiation," *Org. Chem. Curr. Res.*, vol. 4, no. 2, 2015.

[40] K. Sohail, I. U. Khan, Y. Shahzad, T. Hussain, and N. M. Ranjha, "Ph-sensitive polyvinylpyrrolidone-acrylic acid hydrogels: Impact of material parameters on swelling and drug release," *Brazilian J. Pharm. Sci.*, vol. 50, no. 1, pp. 173–184, 2014.

[41] J. Yu *et al.*, "Superabsorbent Polymer Properties and Concentration Effects on Water Retention under Drying Conditions," *Soil Sci. Soc. Am. J.*, vol. 81, no. 4, pp. 889, 2017.

[42] B. Kim, "Effects of pH/temperature on the swelling behavior and rheological properties of hydrogel," Ph.D, University of Southern California, 2010.

[43] N. Vishal Gupta and H. G. Shivakumar, "Investigation of Swelling Behavior and Mechanical Properties of a pH-Sensitive Superporous Hydrogel Composite," *Iran. J. Pharm. Res.*, vol. 11, no. 2, pp. 481–493, 2012.

[44] E. J. R. Rodrigues, P. J. O. Sebastião, and M. I. B. Tavares, "1H time domain NMR real time monitoring of polyacrylamide hydrogels synthesis," *Polym. Test.*, vol. 60, no. September, pp. 396–404, 2017.

[45] T. Wang and S. Gunasekaran, "State of water in chitosan-PVA hydrogel," *J. Appl. Polym. Sci.*, vol. 101, no. 5, pp. 3227–3232, 2006.

[46] M. Zhou, J. Zhao, W. Pu, X. Wang, and Y. Yang, “Synthesis and characterization of salt resistance hydrogel microspheres by inverse suspension polymerization,” *E-Polymers*, vol. 12, pp. 84–95, 2012.

[47] I. I. Muhamad, S. a Asgharzadehahmadi, D. N. a Zaidel, and E. Supriyanto, “Characterization and Evaluation of Antibacterial Properties of Polyacrylamide Based Hydrogel Containing Magnesium Oxide Nanoparticles,” *Int. J. Biol. Biomed. Eng.*, vol. 7, no. 3, pp. 108–113, 2013.

Appendix A

A.1. FTIR Spectrums of Poly Acrylamide Hydrogels

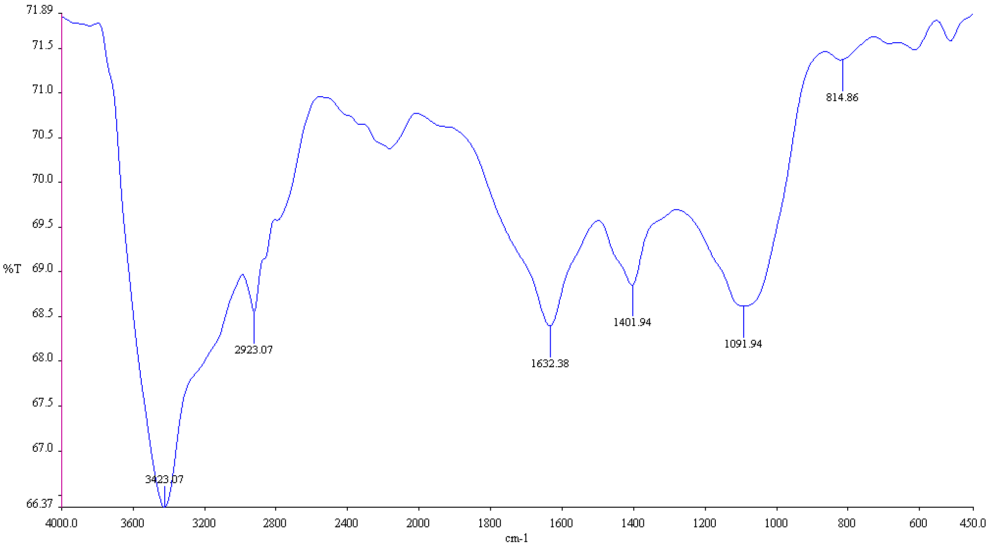


Figure A.1: FTIR result for poly acrylamide hydrogel used in the second run.

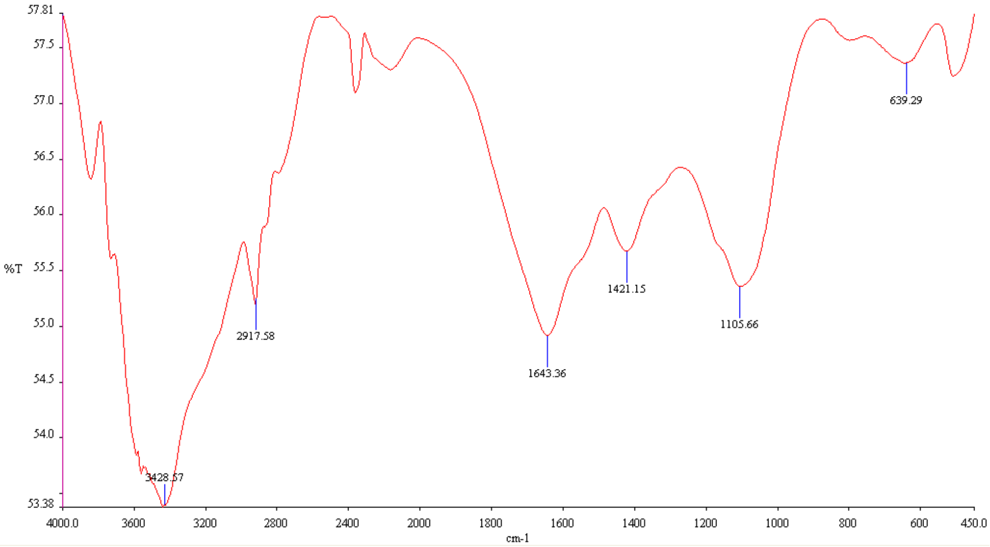


Figure A.2: FTIR result for poly acrylamide hydrogel used in the third run.

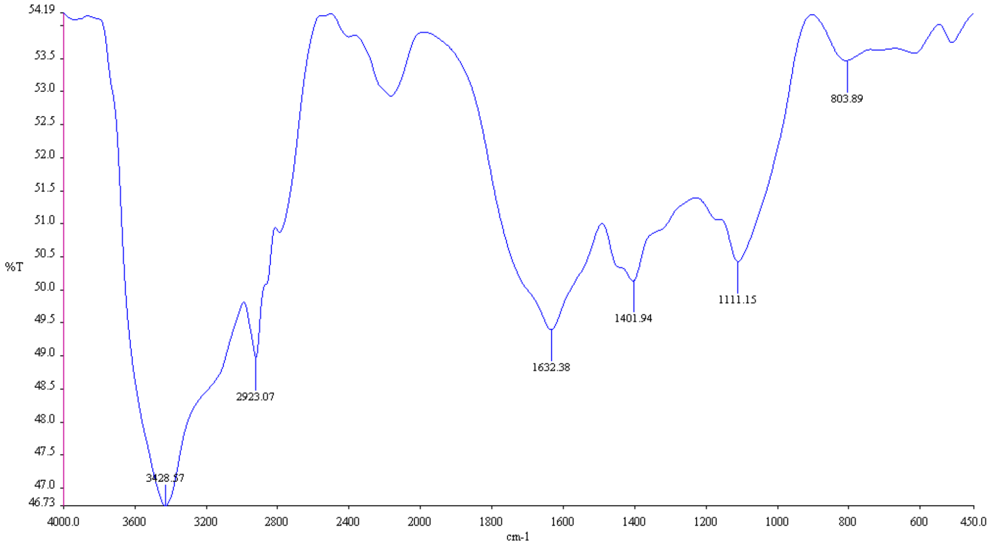


Figure A.3: FTIR result for poly acrylamide hydrogel used in the fourth run.

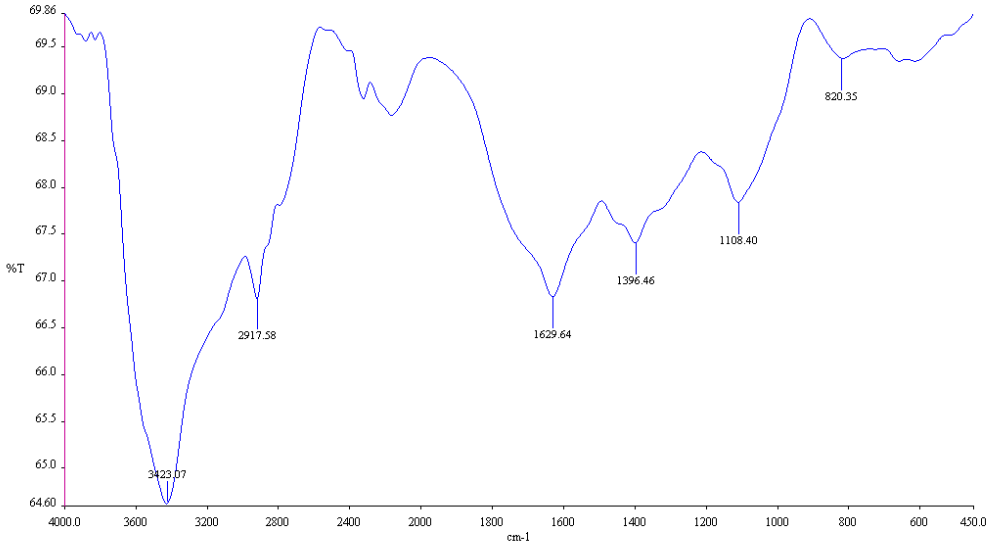


Figure A.4: FTIR result for poly acrylamide hydrogel used in the fifth run.

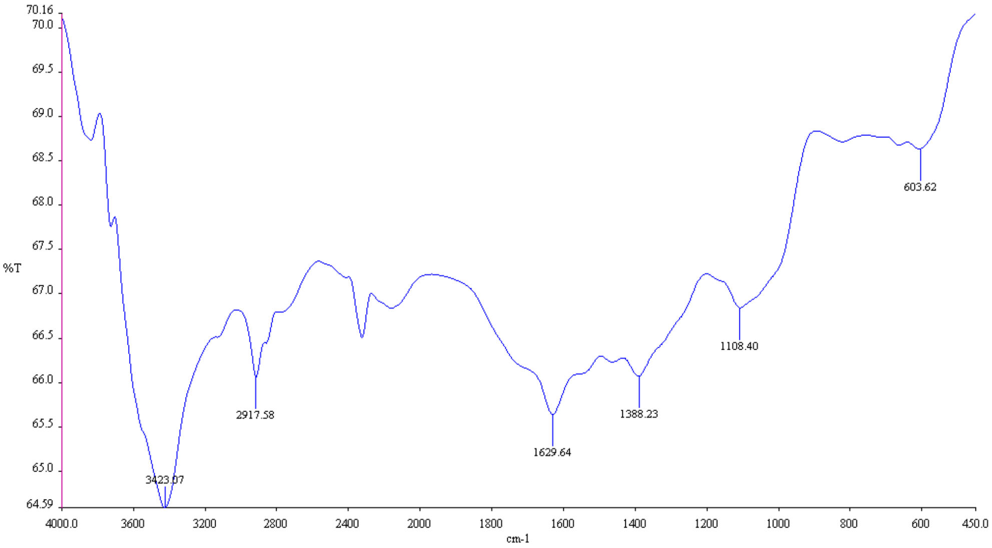


Figure A.5: FTIR result for poly acrylamide hydrogel used in the sixth run.

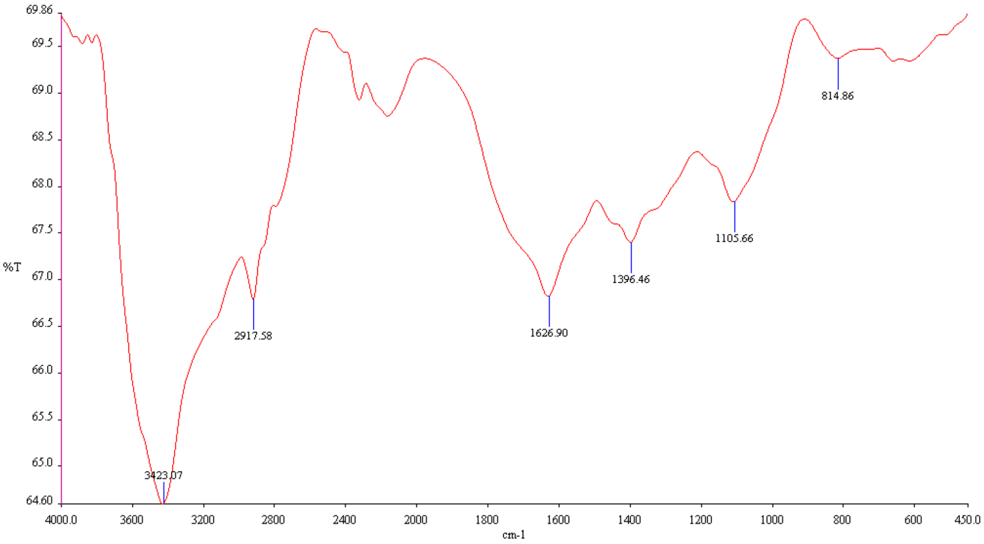


Figure A.6: FTIR result for poly acrylamide hydrogel used in the seventh run.

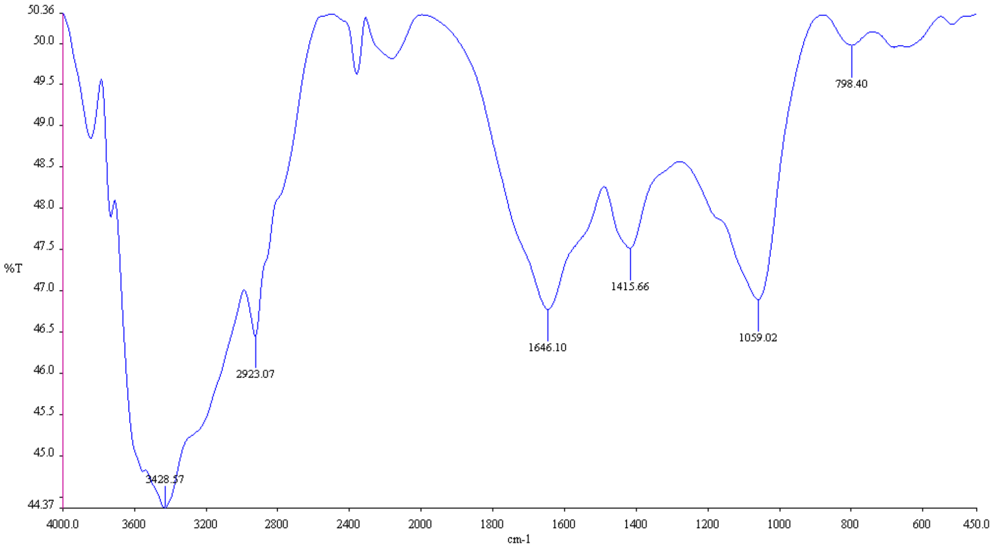


Figure A.7: FTIR result for poly acrylamide hydrogel used in the eighth run.

Vita

Noun Abdalla Abdelraouf Abdelwahab was born in 1991, in Khartoum, Sudan. She completed her primary education in Villa Gilda School and secondary education in Sisters` School. She enrolled in University of Khartoum to graduate with a bachelor degree of chemical engineering in September 2013.

After graduation, Ms. Abdelwahab worked for two years as a calibration engineer in Nano for measurement and calibration center in Sudan. In spring 2016, she joined the MSc program of chemical engineering in American University of Sharjah where she was awarded full graduate teaching assistant.

Ms. Abdelwahab is the first author for submitted paper to *Journal of Porous Media* (it was approved for online publication), entitled "*The Effect of the Membrane Thickness on the Performance of Direct Methanol Fuel Cell*".