

## Preparation of Hydrogels Based Methacrylamid by Thermal Method for Water Adsorption and Changing Rheological Properties of Bentonite-Base Drilling Mud

Shokoufeh Abbasi<sup>1</sup>, Alireza Fazlali<sup>2\*</sup>, Maryam Adimi<sup>1</sup>, Amir H Mohammadi<sup>3,4\*</sup>

<sup>1</sup> Department of Chemical Engineering, Islamic Azad University- Farahan Branch, Farahan, Iran

<sup>2</sup> Department of Chemical Engineering, Faculty of Engineering, Arak University, Arak, Iran

<sup>3</sup> Institut de Recherche en Génie Chimique et Pétrolier (IRGCP), Paris Cedex, France

<sup>4</sup> Discipline of Chemical Engineering, School of Engineering, University of KwaZulu-Natal, Howard College Campus, King George V Avenue, Durban 4041, South Africa

Received March 29, 2020; Accepted June 1, 2020

---

### Abstract

The purpose of this work was to study the performance of hydrogels based on methacrylamide (co-monomer with acrylic acid) for water adsorption and changing rheological properties of bentonite-base drilling mud. For this purpose, the hydrogel was prepared by the thermal-solution method and radical polymerization. The effects of four factors consisting of monomer concentration, temperature, solution concentration of crosslinking agent and methacrylamide/acrylic acid molar ratio on the percentage of hydrogel swelling and viscosity of drilling mud were investigated and it was found that the most important factor is the concentration of monomer for both parameters. To observe the effects of various factors, Taguchi experimental design method was used and the results were analyzed by Minitab 16.2 software. The influence of hydrogel concentration on drilling mud was studied and results indicated that the increasing concentration of hydrogel in the mud, increases the drilling mud viscosity and the viscosity reaches to 192.3 centi-poise (for 300 ppm hydrogel concentration). It was also found that the hydrogel swelling time to reach equilibrium content is about 2 hours. Structure and properties of the hydrogels were tested by FTIR spectroscopy method and DSC thermal analysis and the results indicated that poly (acrylamide-co-acrylic acid) hydrogels had been synthesized very well.

**Keywords:** Hydrogel; FTIR spectroscopy; DSC thermal analysis; Swelling; Viscosity; Drilling mud.

---

## 1. Introduction

Hydrogels have water-swollen, cross-lined polymeric structure and behave mechanically similar to highly swollen elastomer [1]. Hydrogels have gained critical attentions due to their remarkable guarantee for biomechanical provisions. Hydrogels would three dimensionally crosslinked hydrophilic polymer networks that have proficiency with hold an expansive volume for water in the swollen state. [2]. Depending on the type of monomers (i.e. ionic or neutral) incorporated in the gels, they can be made to respond to a variety of external environmental changes such as pH, ionic strength, temperature or specific chemical compounds [3]. These materials are of great paramount due to their promising applications such as controlled drug-distribution systems, artificial muscles [3], sensor systems [4] and in tissue engineering [5], etc. These applications mainly depend upon the swelling behavior of these polymeric hydrogels, which in turn, are controlled mainly by the crosslinking density [1-2].

Huglin *et al.* [6] investigated the swelling behavior of various hydrogels based on the balance of acrylic acid (AAc) as a hydrophilic moiety and methacrylic acid (MAc) as a hydrophobic moiety, and concluded that the swelling ratio was dependent on the amount of acid group and methyl group in the hydrogel. They reported that acid group in AAc increased the swelling ratio, and hydrophobic property of hydrogel was due to the methyl group of MAc, and also reported that the ionization of sulfonic group in 2-acrylamide-1-methyl-2-propane sulfonic

acid (AMPS) to various pH values also increased the swelling ratio. Slawinski *et al.* [7] developed seeded emulsion polymerization of styrene incorporated with acrylic acid in latex particles. They examined the distribution of AAc in the system, from three loci, aqueous phase, the surface of particle, and inside particle (submerged between polystyrene chains). The distribution of AAc was dependent on the pH value of solvent and the feed concentration of AAc – showed the highest AAc concentration on the particle surface at pH 2.5, and the average diameter of their final particles was 102 nm.

The ability of hydrogels to absorb water arises from hydrophilic functional groups attached to the polymeric backbone, while their resistance to dissolution arises from cross-links between network chains [8]. Many substances, both clearly going on and artificial, fit the definition of hydrogels. During last two decades, herbal hydrogels had been gradually replaced via artificial hydrogels that have lengthy carrier existence, high capacity of water absorption, and excessive gel electricity [9-10]. Incidentally, artificial polymers normally have properly-defined structures that can be modified to yield tailor capable degradability and capability [5]. Hydrogels camwood a chance to be synthesized from purely manufactured parts. Also, it will be stable in the states about sharp and solid fluctuations of temperatures [11]. Hydrogels may be synthesized in a number of "classical" chemical ways [12]. Those consist of one-step strategies like polymerization and parallel cross-linking of multifunctional monomers, in addition to a couple of step approaches related to synthesis of polymer molecules having reactive agencies and their next pass-linking, probable also by using reacting polymers with suitable go-linking retailers [12-13]. Those polymer specialist could outline What's more integrate polymer networks with molecular-scale control over structure for example, cross-linking thickness Furthermore for customized properties, for example, biodegradation, mechanical strength, and compound Furthermore living light of jolts. [14].

In summary, a hydrogel is genuinely a hydrophilic polymeric network move-linked in some style to produce an elastic shape. Thus, any technique which can be used to create a cross-linked polymer can be used to produce a hydrogel. Copolymerization/cross-linking free-radical polymerizations need aid regularly utilized to prepare hydrogels toward reacting hydrophilic monomers with multifunctional cross-linkers. [9]. Water-soluble linear polymers of both natural and synthetic origin are cross-linked to form hydrogels in a number of ways [8-9]:

1. Linking polymer chains through substance response.
2. Utilizing ionizing radiation on produce main-chain nothing radicals which could recombine as cross-join junctions.
3. Physical cooperation for example, entanglements, electrostatics, What's more crystallite shaping.

Any of the various polymerization techniques can be used to form gels, including bulk, solution, and suspension polymerization [8]. In general, the three essential analytics parts of the hydrogels preparation would monomer, initiator, and also cross-linker. With control the heat of polymerization and the final hydrogels properties, diluents might be used, for example, such that water or different watery results. Then, those hydrogel impostor needs with make washed will uproot impurities exited starting with the preparation methodology [8-10].

Preparation of hydrogel based on acrylamide, acrylic acid, and its salts by inverse-suspension polymerization and diluted solution polymerization have been also investigated elsewhere [15]. Fewer studies are done on extremely focused answer chemical process of acrylic monomers, that square measure principally proprietary [16]. Chen [17] produced acrylic acid-sodium acrylate superabsorbent through concentrated (43.6 wt%) solution polymerization using potassium persulphate as a thermal initiator.

Hydrogels are normally prepared from polar monomers. Consistent with their beginning materials, they'll be divided into natural compound hydrogels, artificial compound hydrogels, and mixtures of the 2 categories. From a preceding purpose of read, they'll be obtained by graft chemical action, cross-linking chemical action, networks formation of soluble compound, and radiation cross-linking, etc. [8]. There are many sorts of hydrogels; principally, they're gently cross-linked copolymers of propenoate and propenoic acid, and grafted starch-acrylic acid polymers ready by inverse suspension, emulsion chemical process, and answer chemical process [8-9].

Ionizing high energy radiation, like gamma rays [18] and electron beams [19], has been used as an initiator to prepare the hydrogels of unsaturated compounds. The irradiation of liquid chemical compound solution leads to the formation of radicals on the chemical compound chains. Also, radiolysis of water molecules leads to the formation of group radicals, that additionally attack the chemical compound chains, leading to the formation of macro-radicals [18]. Recombination of the macro-radicals on completely different chains ends up in the formation of valence bonds, so finally, a cross-linked structure is made. samples of polymers crosslinked by the radiation technique are poly (vinyl alcohol), poly (ethylene glycol), and poly (acrylic acid) [20]. The main benefit of the radiation initiation over the chemical initiation is that the production of comparatively pure and initiator-free hydrogels [18].

In summary, the functional features of an ideal hydrogel material suggested by various researchers, can be listed as follows [20]:

- The highest absorption capability (maximum equilibrium swelling) in saline.
- Desired rate of absorption (preferred particle size and porosity) looking on the applying demand.
- The highest permeability underneath load (AUL).
- The lowest soluble content and residual chemical compound.
- The lowest value.
- The highest sturdiness and stability within the swelling setting and through the storage.
- The highest biodegradability while not formation of toxicant species following the degradation.
- pH-neutrality once swelling in water.
- Colorlessness, odorlessness, and absolute non-toxic.
- Photo stability.
- Re-wetting capability (if required) the colloidal gel must be able to repay the imbibed resolution or to take care of it; looking on the applying demand (e.g., in agricultural or healthful applications) [15].

Khodja *et al.* [21] optimized drilling conditions in the Hassi Messaoud Algerian field and investigated rheological and filtration characteristics of water-based muds with different polymers. They strongly minded that the adding of anionic polymers polyanionic cellulose (PAC) and xanthenes resins (XC) to drilling mud increased the viscosity of the solutions. Also, it absolutely was found that the consistence vary is higher for KCl compound solutions than for polymers, which the action of part hydrolyzed polyacrylamide compound (PHPA) might avoid disintegration of sedimentary rock material. Though some publications are dedicated to the results of some totally different polymers on lubricator behavior, effects of natural hydrogels, like chitosan gel, on lubricator properties stay unreported.

It is clear that there are a few studies about impact of various parameters on swelling ratio ability and drilling mud viscosity if hydrogels are added. In this regard, a gel composite based on methacrylamid (co-monomer with acrylic acid) for water adsorption application was synthesized by radical polymerization as chemically crosslinking in the present work. The effect of various experimental conditions on the rheological and swelling behavior of the hydrogels such as the effect of temperature, monomer concentration, concentration of crosslinked solution and methacrylamid- acrylic acid ratio were carefully investigated. For this purpose, Taguchi design experiment method was employed to evaluate and optimize hydrogel preparation parameters.

## 2. Materials and method

### 2.1. Materials

The monomers methacrylamide (MAAm), and acrylic acid (AAc) were supplied from Merck, Darmstadt, Germany. The crosslinker N, N-methylene bisacrylamide (MB), the initiator potassium persulphate (KPS) and catalyst-initiator tetramethylethylenediamine (TEMED) were also purchased from Merck. The montmorillonite (Bentonite) based drilling fluid and poly ethylene glycol (PEG) were supplied from Sigma-Aldrich, St. Louis, USA. De-ionized water having 18.2

MΩ.cm resistivity was used for the preparation of all solutions. The monomer MAAM was re-crystallized in methanol to remove the inhibitor.

## 2.2. Hydrogel preparation

Primarily, the specified amount of acrylic acid and methacrylamide were individually dissolved in distilled water to give a solution of 50% wt. with total volume of 5 mL. The solutions were completely stirred (Stirrer, XT 220 A, Perisca) for 15 min. Next, 10% wt. of PEG to monomers ratio was added to the solution and it was again stirred for 15 min. 0.1 g of cross-linker MB was added to 5 mL of DI-water to prepare a solution which should be mixed with solution of the previous step. To this solution definite amount of KPS solution (30%wt.) and TEMED solution (30% wt.) were added drop wise consequently. Final solution was transferred into PVC straws, each of diameter 5.30 mm and kept in an electric oven (SHFH22ST, Shimaz Co., Iran) at 40°C for a period of 30 min. After the chemical change was over, the gels were turn over little items, every of length a pair of  $0.54 \pm 0.02$  cm, equilibrated in water to get rid of the unreacted salts then dried in an exceedingly dust-free chamber until they earned constant weight. The length, diameter and mass of dry samples were found to be a pair of  $0.25 \pm 0.02$ ,  $0.46 \pm 0.03$  and  $0.1875 \pm 0.0108$ , severally. Here, it's price mentioning that issues for choosing the feed compositions within the gift study were the solubility of the monomers, and also the form stability of the swollen gels within the equilibrium state. The final dry samples were added to drilling fluid with different weight percent to study its swelling ratio and thermal properties.

The gel preparation procedure via radiation technique was almost like the procedure employed by the heating method; but, at a later stage of the procedure, crosslinker and instigator weren't added. Indeed, they weren't necessary for this technique. even so, ammonia sulfate was added so as to stop the assembly of homopolymer. methyl alcohol was used as solvent and therefore the extraction time was of seventy two hours.

## 2.3. Swelling determination

Completely dried samples were placed in 500 mL of buffer solution with an ionic strength of 0.05 M at 30°C. The swollen gels were taken out at regular time-intervals, wiped superficially with filter paper to get rid of the surface water, weighed then place within the same bathtub. The mass measurements were continuing until the gels earned constant weight. The % mass swelling resolve mistreatment the subsequent expression [17]:

$$Swelling_M(\%) = \frac{w_1 - w_0}{w_0} \times 100 \quad (1)$$

where  $w_1$  and  $w_0$  are the initial mass and mass at different time-intervals, severally.

All the experiments were dispensed with five samples and also the average values were reported within the knowledge. Preparations of buffer solutions: NaCl/HCl, pH 1.2–2.0; HCl/KHC<sub>6</sub>H<sub>4</sub>(COO)<sub>2</sub>/NaOH, pH 3.0–5.0; NaOH/KH<sub>2</sub>PO<sub>4</sub>/Na<sub>2</sub>HPO<sub>4</sub>, pH 6.0–7.4. The ionic asset was preserved at 0.1 mol/l by addition certain amount of NaCl into the buffer solutions [9, 11].

## 2.4. Design of experiments using orthogonal array by Taguchi methodology

It is worth mentioning that the swelling ratio and rheological behavior of prepared drilling fluid depend upon various significant parameters viz. molar ratio of methacrylamid to acrylic acid, temperature (°C), monomer concentration (ppm) and crosslinker loading (g/5mL). Hence, it is imperative to analyze the parametric effects on swelling ratio and rheological property and their optimization to obtain drilling fluid of desired performance. In order to research such method, Taguchi developed a brand new technique to optimize the result of parameters on mean and variance of performance characteristics [22]. This technique usually uses statistical technique to improve the process situation. The technique is extra advantageous over "one issue at a time" experiments because it provides thorough info regarding interaction of parameters and optimized condition will be determined at intervals only a few

experiments [23]. This methodology uses orthogonal array for coming up with of the experiments. The tactic estimates the foremost influential parameters touching the standard of the merchandise with minimum range of experimental runs thereby reducing precious time and resources. In the present study, L9 array was chosen and different level of each parameter is summarized in Table 1. These levels were selected founded on our earlier work and introductory experiments [14]. The number of experimental runs  $N$  depends upon the number of chosen parameters  $P$  and their levels  $L$ . It is evaluated by Eqn. (2).

$$N = (L - 1)P + 1 \quad (2)$$

Table 1. Selected process parameters and their values at different levels

Parameters	Levels		
	1	2	3
Molar ratio of methacrylamid to acrylic acid	0.5	1	1.5
Temperature (°C)	25	40	55
Monomer concentration (ppm)	10	30	50
Crosslinker concentration (g/5mL)	0.05	0.1	0.15

## 2.5. Rheological measurements

Viscometer bath measurement (KV-6 model, STANHOPE-SETA) was used to characterize the rheological properties of cross-linked methacrylamide hydrogels which was added to drilling fluid. The Seta KV-6 offers the user a high exceptional and sturdy declare kinematic viscosity determinations. Immoderate precise temperature balance Associate in nursing uniformity become performed with an enclosed superior Thermostat and heating and stirring device. All internal parts had been of stainless-steel creation to form bound long term strength and appropriate to be used with either oil, Sloane fluid or water bathtub media. The huge fifty cubic decimeter potential ensures minimum temperature restoration time once loading of bath, enhancing pattern output. Digital temperature control and inbuilt cold water cooling coil provided accurate and stable test temperatures from ambient to 150°C ±0.01°C.

## 3. Results and discussion

### 3.1. Taguchi design and ANOVA

#### 3.1.1. Swelling ratio

Based on the Taguchi design, the effects of the independent variables on the swelling ratio and rheological behavior of samples were analyzed using ANOVA. The analysis indicated that the predicted model was linear and all of the main parameters had significant effects on the estimated model which results were shown in Table 2.

Table 2. Experimental runs of the Taguchi design and responses for swelling ratio and drilling mud viscosity

No.	Methacrylamid to acrylic acid molar ratio	Parameters			Responses	
		Temperature (°C)	Monomer (ppm)	Crosslinker (g/5mL)	Swelling ratio (w/w <sub>0</sub> )	Drilling mud viscosity (cP)
1	0.5	25	10	0.05	564	51.4
2	1	40	10	0.1	705	69.7
3	1.5	55	10	0.15	564	105.7
4	1.5	40	30	0.05	750	90.1
5	1	55	30	0.1	1128	154.7
6	0.5	25	30	0.15	497	104.1
7	0.5	55	50	0.05	1184	194.1
8	1.5	25	50	0.1	846	147.9
9	1	40	50	0.15	1241	185.1

The mean values in terms of S/N ratio for all the four factors are depicted in Fig. 1 with main effects of the parameters on the swelling ratio (w/w<sub>0</sub>) response. The higher response

represents the best level of each factor and was interpreted as optimized value for the operational parameter. The analysis stated for two parameters called monomer concentration and temperature, the highest values in, respectively, 50 ppm and 55°C are positively affecting on swelling ratio. However, the lowest methacrylamid to acrylic acid molar ratio (0.5) has the most impact on swelling ratio. On the other hand, crosslinker concentration had dual impact on swelling as seen in Fig. 1.c. Thus, the second level of crosslinker concentration that had the most S/N ratio, was selected as optimized value for increasing swelling ratio.

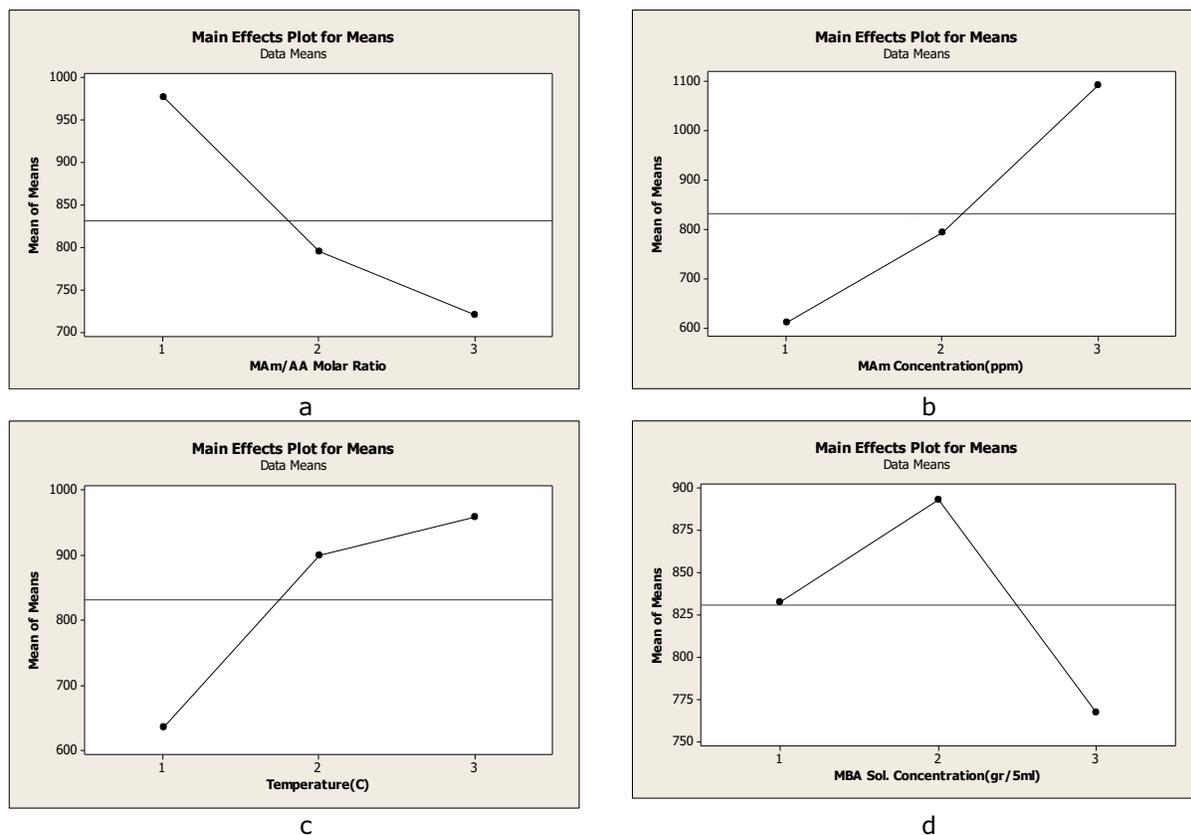


Figure 1. (a) Effect of methacrylamid to acrylic acid molar ratio on swelling ratio, (b) Effect of monomer concentration on swelling ratio, (c) Effect of crosslinker concentration on swelling ratio and (d) Effect of temperature on swelling ratio

Analysis of variance was made for the experimental data to distinguish the significant consequence of factors to response. An F-test was calculated for experimental results and compared with the critical value. ANOVA results are presented in Table 3. As is evident from the table, the initial metal concentration has the biggest add of squares indicating it because the most influential operational parameter whereas compared to others. On the idea of the calculated F-values, no parameter has applied mathematics significance at ninety fifth confidence level. In this regard, Table 4 shows the optimized value of each parameter which has the most impact on swelling ratio increasing.

Table 3. ANOVA for swelling ratio in L9 orthogonal array design

Factors	SS	MS	DOF	F-value	P-value	PC	Rank
Monomer (ppm)	351603	175801	2	3.45	0.101	53.5	1
Crosslinker (g/5mL)	23701	11850	2	0.11	0.896	3.6	4
Temperature (°C)	177098	88549	2	1.11	0.390	26.9	2
Methacrylamid to acrylic acid molar ratio	105313	56656	2	0.57	0.592	16	3
Total	657714	332856	8			100	

SS: Sum of squares; MS: Mean square; DOF: Degrees of freedom; F: Fischer's ratio; PC: Percentage contribution

Table 4. Optimized values for preparation of the best hydrogel for swelling

Factors	Optimized value	Optimized level
Monomer (ppm)	50	3
Crosslinker (g/5mL)	0.1	2
Temperature (°C)	55	3
Methacrylamid to acrylic acid molar ratio	0.5	1

### 3.1.2. Drilling mud viscosity

The analysis of variance for all factors which affect the hydrogel- based drilling mud viscosity is also stated in Table 5. Response value for the calculated signal-to-noise ratios and the ranks of factors for drilling mud viscosity are presented in Fig. 2 and Table 5, respectively. From the observation of the ranks obtained for each factor, it is evident that monomer concentration is the most influential factor for the two responses swelling ratio and drilling mud viscosity, whereas methacrylamid to acrylic acid molar ratio and crosslinker concentration were the least influential factors for drilling mud viscosity and swelling ratio, respectively. Because, the higher response represents the best level of each factor (larger is better) and was interpreted as optimized value for the operational parameter. In this regard, the optimized values for preparation of the best hydrogel for addition into drilling mud are presented in Table 6.

Table 5. ANOVA for drilling mud viscosity in L9 orthogonal array design

Factors	SS	MS	DOF	F-value	P-value	PC	Rank
Monomer (ppm)	15205	7602	2	9.06	0.015	75.12	1
Crosslinker (g/5mL)	597	299	2	0.09	0.914	2.95	3
Temperature (°C)	4063	2031	2	0.75	0.511	20.07	2
Methacrylamid to acrylic acid molar ratio	376	188	2	0.06	0.945	1.86	4
Total	20241	10120	8			100	

SS: Sum of squares; MS: Mean square; DOF: Degrees of freedom; F: Fischer's ratio; PC: Percentage contribution

Table 6. Optimized values for preparation of the best hydrogel for addition into drilling mud

Factors	Optimized value	Optimized level
Monomer (ppm)	50	3
Crosslinker (g/5mL)	0.15	3
Temperature (°C)	55	3
Methacrylamid to acrylic acid molar ratio	0.5	1

Percentage contributions of each factor toward responses are presented in Fig. 3. The contribution of monomer concentration was greatest for both responses swelling ratio and drilling mud viscosity, respectively. On the other hand, the crosslinker concentration and methacrylamid to acrylic acid molar ratio (MAm/AA molar ratio) were least for swelling ratio and drilling mud viscosity, respectively.

The effect of time on the water uptake behavior of the sample that was optimized by Taguchi method as the most swollen hydrogel. All hydrogels swelled rapidly and reached equilibrium within 140 min in addition to the drilling mud. With increasing methacrylamid content, the water uptake ability of the hydrogels increased, and the sorption time to equilibrium also extended. This was accredited to the hydrophilicity of methacrylamid and hydrophilic functional groups accomplished of hydrogen bonding, for example  $-\text{CONH}$  and  $-\text{CONH}_2$ . In general, the equilibrium water content (EWC) of methacrylamid based hydrogels was reported 100–900%, which increased with monomer content (methacrylamid). As seen in Fig. 4, sample 10 ppm possessed fewer hydrophilic functional groups than the other hydrogels. Accordingly, 10 ppm retains the smallest amount of water among the samples. No large differences can be seen between 10 ppm and 50 ppm. This performance may be attributed not only to the amount of

the methacrylamid network but also to the quantity of the crosslinking agent having a large amount of water-binding sites, they are accredited to the high crosslinking degree of methacrylamid.

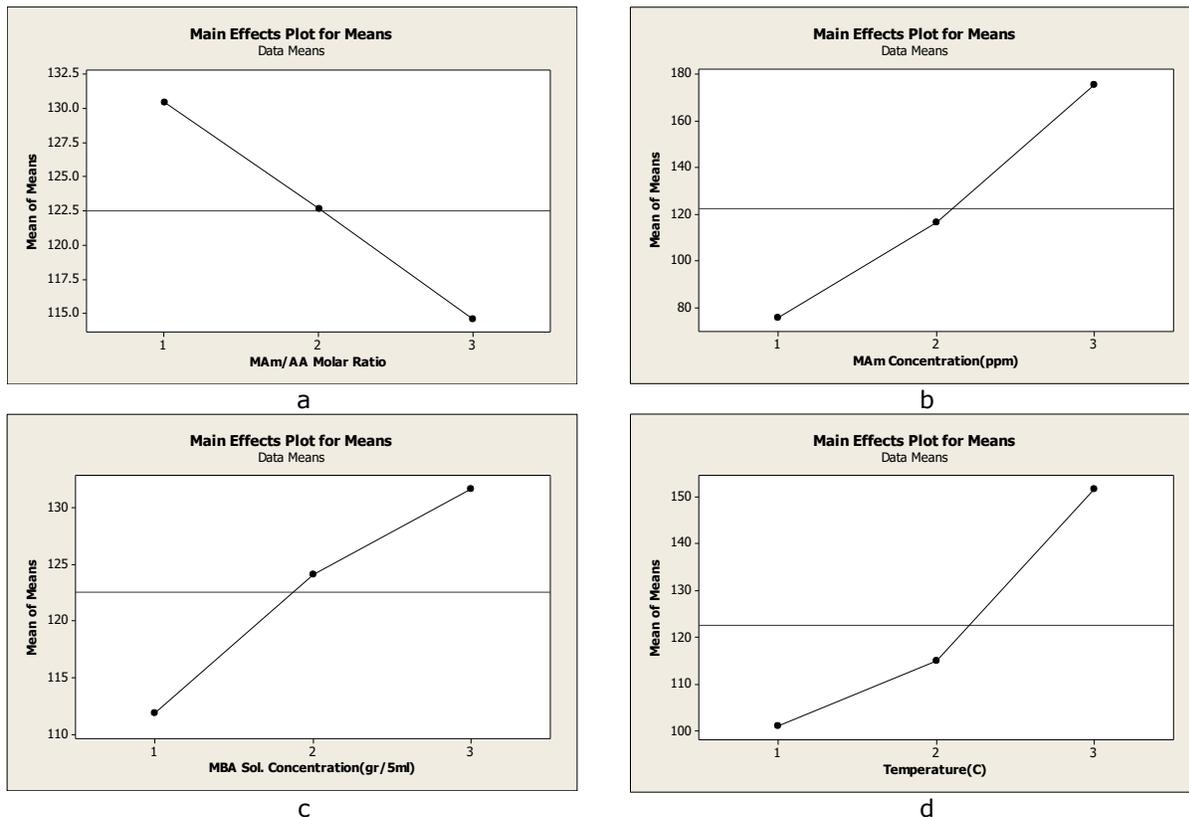


Figure 2. (a) Effect of methacrylamid to acrylic acid molar ratio on drilling mud viscosity, (b) Effect of monomer concentration on drilling mud viscosity, (c) Effect of crosslinker concentration on drilling mud viscosity and (d) Effect of temperature on drilling mud viscosity

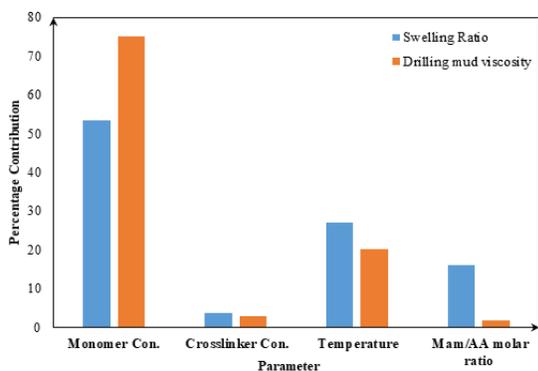


Figure 3. Percentage contribution of effective factors of swelling ratio and drilling mud viscosity

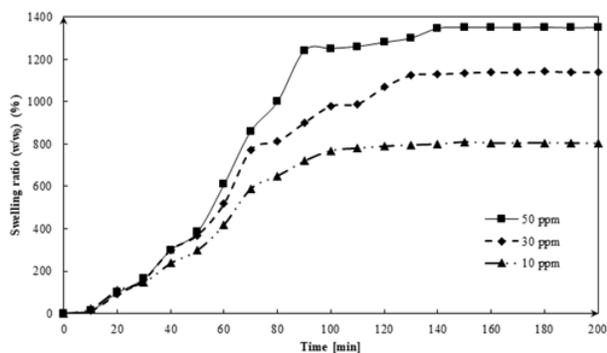


Figure 4. Equilibrium water uptake behavior of optimized hydrogel with various monomer content vs. time

### 3.2. FTIR analysis

In Fig. 5, the FTIR spectra is shown for the optimized hydrogel. The FTIR spectrum displayed wide peak at 3100–3500  $\text{cm}^{-1}$ , which is relevant to formation of methacrylamid copolymer and acrylic acid. These peaks are ascribed to O-H and N-H groups. C-H stretching vibration displayed two bands, with those at 2740  $\text{cm}^{-1}$  and 2900  $\text{cm}^{-1}$  while the band at 1742  $\text{cm}^{-1}$  which was the result of the vibration of C=O bond that well-known carboxyl groups. The

1580  $\text{cm}^{-1}$  and 1448  $\text{cm}^{-1}$  peaks are characteristics of the CH groups from the backbone of AAm units, while the peak at 2180  $\text{cm}^{-1}$  demonstrates the  $-\text{C}-\text{N}$  bond related to crosslinker and methacrylamid. In summary, formation of co-polymer is proven by the presence of peaks at 3500  $\text{cm}^{-1}$  to 3100  $\text{cm}^{-1}$  peaks, which are ascribed to the O-H- and N-H stretching vibrations.

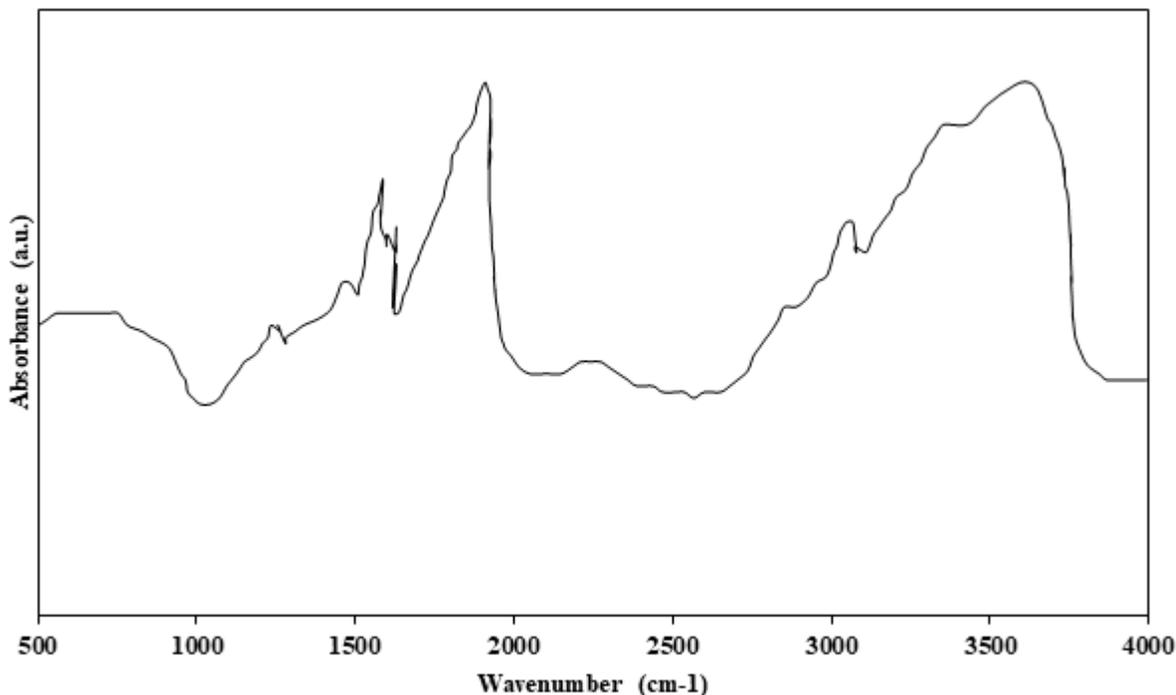


Figure 5. FTIR spectra of optimized sample related to swelling ratio

### 3.3. Effect of concentration on rheological property

Carboxymethyl cellulose (CMC) and xanthenes (XC) resins are often used in drilling fluids to increase the viscosity [24]. Fig. 6 shows viscosity of hydrogel based drilling mud prepared by thermal processes at different concentrations. This figure proves that, at low concentrations, lubricant will increase consistency slightly over gel samples, while at high concentrations hydrogels increase this parameter way more than CMC and XC that's pronounced in radiation ready hydrogels.

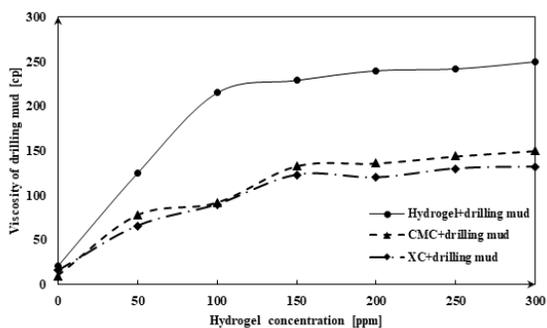


Figure 6. Concentration (ppm) effect of prepared hydrogels, CMC, and XC polymers upon viscosity (cP) of drilling mud

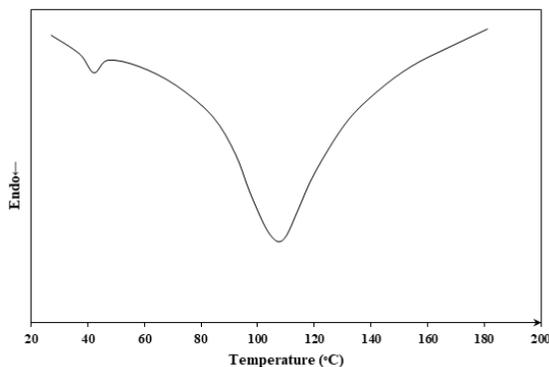


Figure 7. DSC Thermograms of swollen optimized hydrogel

Fig. 7 demonstrates the DSC thermograms of water swollen optimized hydrogel. Two melting peaks within the optimized gel may be seen within the DSC curve, indicating that free water and cooling certain water exist within the gel. As a rule, DSC was used to determine the amount of free water that is not bound by hydrogen bonding. Bound water attributed to hydrogen bonding with the methacrylamid chains is expressed as the difference between the total water and the free water. The endothermic peaks appearing around 35–40°C, shown in Fig. 7, were accredited to the attendance of free water in the hydrogels. It can be argued; the amount of free water can be increased with monomer content in the hydrogel. This indicated that the increase of EWC with monomer content is attributed mainly to the free water content in the hydrogel.

#### 4. Conclusion

In this paper, hydrogels have been formed through thermal and radiation preparation processes to change rheological properties of drilling mud. The influence of four factors consist of monomer concentration, temperature, solution concentration of crosslinking agent and methacrylamide/acrylic acid molar ratio on the percentage of hydrogel swelling and viscosity of drilling mud were examined and it was found that the most important factor was the concentration of monomer for both. To observe the effects of various factors, Taguchi experimental design method was used and the results were investigated by Minitab 16.2 software. The influence of hydrogel concentration on drilling mud was examined and results indicated that the increasing concentration of hydrogel in the mud, increases the drilling mud viscosity and the viscosity reaches to 192.3 cP (300 ppm hydrogel concentration). According to other results of this study, viscosity increased significantly with hydrogel concentration so that at low concentrations, drilling mud increases viscosity slightly more than hydrogel samples, while at high concentrations hydrogels increase this parameter much more than CMC and XC. DSC thermograms of water swollen optimized hydrogel showed that bound water attributed to hydrogen bonding with the methacrylamid chains can be expressed as the difference between the total water and the free water. The endothermic peaks seeming were accredited to the incidence of free water in the hydrogels. It can be indicated that amount of free water can be enlarged by monomer content in the hydrogel. This indicated that the increase of EWC with monomer content is attributed mainly to the free water content in the hydrogel.

#### References

- [1] Zaharia A, Sarbu A, Radu A-L, Jankova Atanasova K, Daugaard AE, Hvilsted S, Perrin F-X, Teodorescu M, Munteanu C, Fruth-Oprisan V. Preparation and characterization of polyacrylamide-modified kaolinite containing poly [acrylic acid-co-methylene bisacrylamide] nanocomposite hydrogels. *Applied Clay Science*, 2015; 103: 46-54.
- [2] Zheng Y, Gao T, and Wang A. Preparation, Swelling, and Slow-Release Characteristics of Superabsorbent Composite Containing Sodium Humate,. *Industrial & Engineering Chemistry Research*, 2008; 47: 1766-1773.
- [3] Hoare TR and Kohane DS. Hydrogels in drug delivery: Progress and challenges. *Polymer*, 2007; 49: 1993-2007.
- [4] Fernandes MS, Dias NS, Silva AF, Nunes JS, Lanceros-Méndez S, Correia JH, Mendes PM. Hydrogel-based photonic sensor for a biopotential wearable recording system. *Biosensors and Bioelectronics*, 2010; 26: 80-86.
- [5] El-Sherbiny IM and Yacoub MH. Hydrogel scaffolds for tissue engineering: Progress and challenges. *Global Cardiology Science & Practice*, 2013; 2013(3): 316-342.
- [6] Huglin MB, Liu Y, and Velada J. Thermoreversible swelling behaviour of hydrogels based on N-isopropylacrylamide with acidic comonomers. *Polymer*, 1997; 38: 5785-5791.
- [7] Slawinski M, Schellekens MAJ, Meuldijk J, van Herk AM, and German AL. Seeded emulsion polymerization of styrene: influence of acrylic acid on the particle growth process. *Journal of Applied Polymer Science*, 2000; 76: 1186-1196.

- [8] Ahmed EM. Hydrogel: Preparation, characterization, and applications: A review. *Journal of Advanced Research*, 2015; 6: 105-121.
- [9] Akhtar MF, Hanif M, and Ranjha NM. Methods of synthesis of hydrogels: A review. *Saudi Pharmaceutical Journal*, 2016; 24(5): 554-559.
- [10] Mathur AM, Moorjani SK, and Scranton AB. Methods for Synthesis of Hydrogel Networks: A Review. *Journal of Macromolecular Science, Part C*, 1996; 36: 405-430.
- [11] Abd Alla SG, Sen M, and El-Naggar AWM. Swelling and mechanical properties of superabsorbent hydrogels based on Tara gum/acrylic acid synthesized by gamma radiation. *Carbohydrate Polymers*, 2012; 89: 478-485.
- [12] Ray D, Gils PS, Mohanta GP, Manavalan R, and Sahoo PK. Comparative delivery of Diltiazem hydrochloride through synthesized polymer: Hydrogel and hydrogel microspheres. *Journal of Applied Polymer Science*, 2010; 116: 959-968.
- [13] Zu Y, Zhang Y, Zhao X, Shan C, Zu S, Wang K, Li Y, Ge Y. Preparation and characterization of chitosan-polyvinyl alcohol blend hydrogels for the controlled release of nano-insulin. *International Journal of Biological Macromolecules*, 2012; 50: 82-87.
- [14] Bergmann NM and Peppas NA. Molecularly imprinted polymers with specific recognition for macromolecules and proteins. *Progress in Polymer Science*, 2008; 33: 271-288.
- [15] Raju KM and Raju MP Synthesis of novel superabsorbing copolymers for agricultural and horticultural applications. *Polymer International*, 2011; 50: 946-951.
- [16] Park K, and Park H. Super-absorbent hydrogel foams. <https://patents.google.com/patent/US20010038831A1/en>.
- [17] Chen J, and Zhao Y. Relationship between water absorbency and reaction conditions in aqueous solution polymerization of polyacrylate superabsorbents. *Journal of Applied Polymer Science*, 2000; 75: 808-814.
- [18] Karadağ E, Saraydın D, and Güven O. Radiation Induced Superabsorbent Hydrogels. Acrylamide/Itaconic Acid Copolymers. *Macromolecular Materials and Engineering*, 2001; 286: 34-42.
- [19] Ajji Z, Mirjalili G, Alkhatab A, and Dada H. Use of electron beam for the production of hydrogel dressings. *Radiation Physics and Chemistry*, 2008; 77: 200-202.
- [20] Zohuriaan-Mehr MJ, and Kabiri AK. Superabsorbent Polymer Materials: A review. *Iranian Polymer Journal*, 2008; 17: 451-477.
- [21] Khodja M, Canselier JP, Bergaya F, Fourar K, Khodja M, Cohaut N, Abdelbaki B. Shale problems and water-based drilling fluid optimisation in the Hassi Messaoud Algerian oil field. *Applied Clay Science*, 2010; 49: 383-393.
- [22] Kumar RS, Sureshkumar K, and Velraj R. Optimization of biodiesel production from Manilkara zapota (L.) seed oil using Taguchi method. *Fuel*, 2015; 140: 90-96.
- [23] Su CT. *Quality Engineering: Off-Line Methods and Applications*: CRC Press, 2016.
- [24] Abd El-Mohdy HL. Water sorption behavior of CMC/PAM hydrogels prepared by  $\gamma$ -irradiation and release of potassium nitrate as agrochemical. *Reactive and Functional Polymers*, 2007; 67: 1094-1102.

*To whom correspondence should be addressed: professor Amir H Mohammadi, Institut de Recherche en Génie Chimique et Pétrolier (IRGCP), Paris Cedex, France & Discipline of Chemical Engineering, School of Engineering, University of KwaZulu-Natal, Howard College Campus, King George V Avenue, Durban 4041, South Africa, E-mail: [a.h.m@irgcp.fr](mailto:a.h.m@irgcp.fr) & [amir\\_h\\_mohammadi@yahoo.com](mailto:amir_h_mohammadi@yahoo.com)*