# Synthesis and Application of Hydrogels for Oil-Water Separation

Hashmi, Saud; Mushtaq, Asim<sup>\*+</sup>; Ahmed, Rafiq; Khan, Raza Muhammad

Polymer and Petrochemical Engineering Department, NED University of Engineering & Technology, Karachi, Sindh, PAKISTAN

### Ali, Zaeem Uddin

Chemical Engineering Department, NED University of Engineering & Technology, Karachi, Sindh, PAKISTAN

ABSTRACT: A cotton-based hydrogel nanocomposite was effectively arranged through free radical graft co-polymerization of a combination of Acrylic Acid (AA), acrylonitrile (AN), and sodium acrylate (NaA) onto the texture pursued by the addition of Ag nanoparticles. Ammonium persulfate (APS) and potassium persulfate (KPS) were utilized as initiators within sight of a crosslinker methylene bisacrylamide (MBA). These samples are characterized by Fourier Transform IinfraRed (FT-IR), and X-Ray Diffraction (XRD) to affirm the hydrogel nanocomposite structure. At first, the influencing factors onto graft polymerization were efficiently enhanced to accomplish a hydrogel with a swelling limit as high as expected under the circumstances. The came about nanocomposite shows overly hydrophilic and superhydrophobic properties. In this manner, the grafted texture, specifically from oil/water, blends separated water with high separation productivity. The impacts of channel type, level of covered hydrogel on cotton, nearness of Ag nanoparticles, extricated oil type, and temperature effect were studied on the hydrogel. Nanocomposite on the partition effectiveness of channels was additionally examined. The as-prepared materials were super hydrophilic and superoleophobic in air and submerged in water. Diesel oil and vegetable oil were used selectively at 10% and 20% volume in water. The separation efficiencies for each were observed on different samples, with and without Ag nanoparticles. The materials can isolate the scope of various oil/water blends (counting immiscible oil/water blends and surfactant-balanced out emulsions) with >97% separation efficiency. Effect of poly AN-CO-NaA and poly AN-co-AA ratios the samples show the same nature, their weight increases with time. The rates were different owing to the monomer ratios. Hence the more hydrophilic groups present, the greater the absorption rate, which shows the characteristics of this poly AN-co-AA grafted hydrogel. Sodium acrylate at different proportions in poly AN-co-NaA was tested, and it can be deduced that hydrophilicity increased with greater proportions of the sodium acrylate. Along these lines, the straightforward and effortless technique has superb potential in various applications such as industrial oil-polluted wastewater and oil spillage clean-up.

KEYWORDS: Oil-water, Nanocomposite, Hydrogel, Hydrophilic, Hydrophobic, Diesel.

1021-9986/2022/12/4075-4088

<sup>\*</sup> To whom correspondence should be addressed. +E-mail address: engrasimmushtag@yahoo.com 14/\$/6.04

# INTRODUCTION

Ecological issues have consistently been an incredible worry to humanity. The bounteous release of modern wastewater and incessant oil slick mishaps produced many oil-water blends and emulsions. These blends and emulsions are destructive to the ecotope like the living space for transient winged creatures and are identified with individuals' generation and living. Oil contamination has caused genuine harm to the earth and the environment on the planet. In this manner, isolating oil and water is profoundly requested. There are numerous treatment techniques for sleek wastewater, for example, natural strategy, flocculation technique, film partition, and adsorption strategy. In any case, the natural technique covers a huge territory and huge activity costs. The flocculation strategy has an enormous yield of optional contamination, the adsorption limit of the adsorbent is constrained, and the recovery is troublesome, which restrains the pragmatic application. Although layer materials are broadly utilized in oil/water detachments, their qualities of being long, tedious, contamination-inclined, and pre-treatment limit their further application. Along these lines, it is essential to grow different procedures and materials with excellent partition proficiency, high strength, and selectivity high for oil-water detachment. Regularly utilized oil-water detachment materials are fundamentally isolated in two kinds, superhydrophobic / superoleophilic materials (indeed oil removing with a particular sort of wetting property of material will rebuff the water stage and pass oil) and superhydrophilic / submerged superoleophobic (removing water from the oil/water mix with the turnaround selectivity of engaging oil materials) [1, 2].

In superhydrophobic-superoleophilic materials, due to their lipophilic nature, the oil beads are challenging to adsorb on the material outside and have poor reusability. The super hydrophilic/submerged superoleophobic material beats this hindrance. Even though super hydrophilic/submerged superoleophobic film for slick wastewater treatment can adequately decrease layer fouling without auxiliary contamination, the nano-covering material is effectively stripped off and once in a while utilized under cruel conditions. Along these lines, it's pressing to set up a superhydrophilic / submerged superoleophobic material with a basic, conservative, and viable technique that can be used under extraordinary circumstances [3, 4]. The tale cotton-based nanocomposite hydrogel arranged in

our investigation will have the option to expel oil from oilwater mixes successfully. Detachment of little oil particles and emulsified oil is particularly troublesome, and persuasive techniques have not been created. Spillages are chiefly skimming, expansion of concoction dispersant, utilization of filtrating medium, and different sorbents. Skimming is usually a recognized technique; however, it is tedious, expensive, and wasteful. Another utilized strategy is an oil dispersant that isolates oil into beads; however, it includes extra dangerous synthetics into the ocean and requires additional isolating methods [3, 4].

Utilizing sorbents and filtrating materials is the promising path to cleaning and recalling oil from oil spills. Over the most recent five years, various exponential developments in the examination identified materials for oil-water detachment. Deliberately created and exceptionally arranged super-wetting surfaces are seen to be valuable for explicitly confining oil and water. In general, exceptional wet materials with specific converse similarities concerning oil or water are the most reassuring materials for specific oil-water divisions. Depending upon the wettability of changed filtrating materials such as metallic cross-sections, and materials/surfaces, polymeric movies grant only a solitary explicit stage to experience. These materials have been widely considered over the most recent couple of years for oil-water detachments, such as polypropylene microfiltration membranes with silica, polyvinylidene fluoride (PVDF) membranes with or without multiwall carbon nanotubes, and polyelectrolyte membranes. However, the complicated procedures for fabricating polymers, the toxicity of reagents, and the high cost of materials and equipment limit their practical applications. Therefore, developing low-cost, ecofriendly, and highly effective membrane materials that can separate emulsified oil/water mixtures is of great importance. Creating a new hydrophilic and submerged oleophobic hydrogel-covered texture can specifically and successfully separate water from oil-water blends, for example, olive, diesel, and unrefined petroleum. Accordingly, the water-evacuating hydrogel-covered texture is a decent up-and-comer in mechanical oil-dirtied water medicines and oil-slick clean-up. In this manner, the basic and easy strategy can be utilized in a useful application, for example, purging wastewater from industry and everyday life and managing oil slick mishaps [5, 6].

In this study, the readiness of a cotton texture covered with hydrogel nanocomposite. Due to their superb waterengrossing and water-holding limits, hydrogels are viewed as a promising contender for structuring novel waterexpelling materials for oil/water partition. This technique benefits presenting joined chains with customized properties for explicit applications. The simplicity of creation, effortless and adaptable utilization of the readied product renders its significance in slickwater medications.

In a relentless journey for improving things, material producers go to bleeding-edge developments that can mishandle the novel jobs of materials. In this work, an intriguing revelation of an alternative model dependent on Ag nanoparticles for oil/water detachment is acquainted with advanced structure materials for oil/water partition that recommends appealing potential applications in mechanical sleek wastewater medications and oil slick clean-up. The progressive amalgamation of conditions for accomplishing the most extreme expanding limit and hence the limit of detachment effectiveness, the impacts of monomers, crosslinker, initiator, and Ag focus were researched. They can specifically and successfully separate water from oil/water blends, for example, diesel and vegetable oil. Along these lines, the water-expelling hydrogel-covered texture is a decent competitor in mechanical oilcontaminated water medicines, and oil slick tidies up [7, 8].

The change of polymers has gotten a lot of consideration as of late. Among the strategies for the adjustment of polymers, grafting is one of the promising techniques. On a basic level, unite co-polymerization is an alluring strategy to confer various practical gatherings to a polymer in the previous quite a long while. There has been expanded accentuation on the uses of joined polymers. Extremist polymerization has been broadly utilized as a joining technique for the readiness of new materials for an assortment of employments. A few starting strategies, physical and substance, permit the development of free radicals on a trunk polymer, either engineered or regular, prompting united copolymer arrangement within sight of a suitable monomer. The adjusted polymers have a bright future, and their improvement is for all intents and purposes [9]. In the chemical process, free radicals are created from the initiators and moved to the substrate to respond with monomers to frame the graft copolymers. Generally, one can think about the generation of free radicals by aberrant or direct strategies. In separation

innovations, a layer might be viewed as a stage that hinders forestall mass development by and large yet permits confined and managed entry of at least one species type through it; for example, it controls the particular exchange of molecules or ions. Distinctive customary methods are accessible in separation science. Yet, separation through layers is favorable and is regularly liked because of benefits, including the minimal expense of the procedure, energy savings, what's more, no necessity for a difference in stage or condition of the dissolvable. In this manner, film-based partition science is a piece of the green mega drive; it has decreased vitality utilization and consequently less natural contamination. The proposed process was selected based on the ease of synthesis and quick reproducibility of the hydrogel-coated cotton; the as-prepared product is versatile for the claimed objective of oil-water separation [10, 11].

#### **EXPERIMENTAL SECTION**

The Archroma Textiles Chemicals sponsored materials are cotton fabric, acrylonitrile (AN), acrylic acid (AA), sodium hydroxide (NaOH), methylene bisacrylamide (MBA), and Rongalite-C. Silver nitrate (AgNO<sub>3</sub>) ethanol was purchased from local suppliers. Table 1 shows materials and their compositions. Raw, pure cotton fabric was used as obtained. Firstly, the fabric was cut into equal-sized circles to accommodate the conical flask for grafting. After sizing the fabric, the samples were placed in a detergent solution for 60 minutes. Soaking of detergent was done to remove impurities and or stains, if any, on the fabric. After detergent washing time was over, the samples were thoroughly washed with tap water for 5 minutes; later, they were cleansed with distilled water and squeezed gently to drain the leftover water from them. After washing, the cotton fabric was placed in an air oven to dry out any moisture remaining on the samples. The oven was kept at 600°C for 20-30 minutes until the fabric was dried, as given in Fig. 1.

#### Preparation of the reaction mixture and grafting

Monomers of known amounts were put into a beaker, a known quantity of the crosslinker was added. Stirred the mixture for some time, then 10ml of water was added, and further stirring was done to make a homogenous solution. Later required quantity of initiator was added and stirred till a homogenous solution was prepared. The as-prepared solution was poured into the conical flask. Then the treated

Sample	Monomer 1 AN/ml	Monomer 2	Initiator	Cross-linker MBA/g	Nano-particles AgNO <sub>3</sub>	Reducing agent Ronglite-C
		NaA/g	APS/g			
1	0.5	1.5	0.075	0.05	0.02	0.0015
2	0.5	1.0	0.075	0.05	0.03	0.0015
3	0.5	2.0	0.075	0.05	0.04	0.0015
		AA/ml	APS/g			
4	0.5	1	0.075	0.05	0.02	0.0015
5	0.5	1.5	0.075	0.05	0.03	0.0015
6	0.5	2	0.075	0.05	0.04	0.0015
		AA/ml	APS/g			
7	0.5	1	0.075	0.11	-	-
8	0.5	1	0.075	0.15	-	-
		NaA/g	APS/g			
9	0.5	1	0.075	0.1	-	-
10	0.5	1	0.075	0.15	-	-
		AA/ml	APS/g			
11	1	1	0.075	0.05	0.02	0.0015
		NaA/g	APS/g			
12	1	1	0.075	0.05	0.03	0.0015
		NaA/g	KPS/g			
13	0.5	1	0.06	0.05	0.03	0.0015
14	1	1	0.06	0.05	0.04	0.0015

Table 1. Materials and their compositions



Fig. 1. Process description

fabric sample was immersed in the same flask. The conical flask was then submerged in the water bath, kept at 100°C to graft copolymer hydrogel. The grafting time was set to 120 minutes. When grafting was over, the grafted fabric was taken out and treated to be freed from any

homopolymer, side products, or contaminants. The synthesized product was well washed with distilled water for 10 minutes. After washing, it was extracted in hot water by water bath at 100°C for 300 minutes to remove present homopolymers that were remained unreacted

during the polymerization process of grafting. Due to heat from the water bath, thermal decomposition of initiators (APS/KPS) was achieved. The sulfate anion radicals created due to thermal decomposition separate hydrogen from the hydroxyl group of the monomers to create corresponding alkoxy macroradicals. These formed alkoxy macroradicals on the active sites of the monomers initiate polymerization reaction of the monomers (AA, AN, NaA), thus leading to graft copolymer. Due to the cross-linking agent (MBA), the synthesized copolymer had a cross-linked structure.

The prepared hydrogels were further treated to produce a cotton-based nanocomposite hydrogel. A solution mixture was prepared with various silver nitrate amounts (AgNO<sub>3</sub>) dissolved in 30ml water. The mixture was then mixed well, and the hydrogel grafted fabric was immersed and kept for 30 minutes. To induce Ag nanoparticles, the fabric from AgNO<sub>3</sub> solution was further transferred to Rongalite-C solution, which was prepared with 2mg of solute dissolved in 30ml water. Here the fabric was also kept for 30 minutes till all or maximum silver nanoparticles were reduced. In this, Rongalite-C was used as a reducing agent that oxidized to create nanocomposite hydrogel. The as-prepared grafted nanocomposite cottonbased hydrogel was ready to use for further experiments.

#### Grafting test

The grafting percent (G) was represented using the following equation;

Grafting % = 
$$\left(\frac{W_g - W_o}{W_o}\right) \times 100$$
 (1)

where;  $W_o$  and  $W_g$  = fabric weights before and after graft co-polymerization. The weight measurements were taken twice to minimize fluctuations on the reading scale.

#### Swelling measurement

The swelling characteristics were recorded for every sample concerning time. Equilibrium swelling was also measured for 30 minutes. The dried fabric was immersed in 200ml of distilled water, and then the weight measurements were taken every 3 minutes till 21 minutes, where the weight showed to be almost constant in that time. The equilibrium swelling was tested for every sample to determine the maximum water absorption capacity of the hydrogel. The equilibrium swelling (ES %) was calculated using the formula;

Equilibrium Swelling % = 
$$\left(\frac{W_s - W_d}{W_d}\right) \times 100$$
 (2)

where;  $W_s$  and  $W_d$  = weight of the swollen fabric and dried fabric, respectively. The effect of silver nanoparticles on equilibrium swelling was also studied. The ES% of a respective sample over the periods of 0, 3, 6, 9, 12, 15, and 18 minutes difference, the ES% increases as the time increases, but there is not adequate change occur with the time duration from 12 minutes to 18 minutes. On the other hand. There is sufficient change experience in ES% with nanoparticle insertion except sample membranes 4, 11, 13, and 14.

#### Oil retention ability

The oil-water separation experiment was carried out by mixing different oil proportions in water. Different oil impacts were also tested. The oil-water emulsions were formed by agitators/magnetic stirrers to create oil-water emulsions. The known quantities of oil/water, as shown in the table, were prepared in beakers and then agitated for 15 minutes at 180 rpm with agitator 2rpm in a magnetic stirrer. The mixture was later passed on through the wet cotton-based grafted hydrogel kept to soak water for 10 minutes. The water selectively permeated over the coated mesh, whereas the oil was repelled and stayed on the surface of the synthesized hydrogels fabric. Times for water to be collected in the measuring cylinder was recorded for the samples, with and without nanocomposites. The separation efficiency is given as;

Separation Efficiency 
$$\% = \left(\frac{m_1}{m_0}\right) \times 100$$
 (3)

where;  $m_o = oil$  mass initially added, and  $m_1 = oil$  mass collected after separation.

# RESULTS AND DISCUSSION FT-IR

In poly AN-co-NaA based samples, the presence of hydrophilic group and silver nanoparticle on the surface of the grafted membrane was tested by FT-IR. Also, the effect of Rongalite-C added for reduction of Ag+ to Ag NPs was observed by taking two different samples with Rongalite-C (Cotton-grafted-AN-co-NaA) and without Rongalite-C (Cotton-grafted-(AN-co-NaA)/Ag). In Figures 2 (a, b), both the samples show the same peaks transmitted at certain wavelengths. The effect of reducing Ag nanoparticles was enough by the presence of -NaOH group from sodium acrylate. Thus, the Rongalite-C effect was not dominant





Fig. 3: Sample for XRD (a) with Rongalite (b) without Rongalite

in the final product. Figure 2 (a, b), the transmittance at wavenumber 3334-3000 cm<sup>-1</sup> was abundant due to the presence of the -OH group at large. The wavenumber 1200-1000 cm<sup>-1</sup> showed C-O-C and C-OH stretches, confirming the presence of hydrophilic groups [1, 3, 7, 11].

## XRD

The XRD of the hydrogel membrane is shown in Figure 3 (a, b). It was observed that the peak for NaOH had the greatest counts at 160, and the Ag peak was smallest at 400. Hence the graph depicts the presence of Ag nanoparticles, which were less than NaOH because Rongalite-C (Cotton-grafted-AN-co-NaA) also possesses Na-OH group; therefore, this group peak was dominant. The sample tested was poly AN-co-NaA hydrogel. As compared to the sample without Rongalite-C (Cotton-grafted-(AN-co-NaA)/Ag), the silver peak was dominant at 400 is shown in Figure 3 (b). Hence the XRD results validate the presence of Ag nanoparticles embedded in the polymer network of the poly AN-co-NaA grafted hydrogel [4, 12, 13].

### Water absorbency concerning time

## Effect of Poly AN-CO-NaA and Poly AN-co-AA Ratios

Different AN-co-NaA and AA-co-AN ratios were tested, and their behavior was observed. As shown in Figure 4 (a), the samples show the same nature, their weight increases with time. However, a significant change is that the swelling rate is different [4, 13, 14].

Figure 4 (b) shows an increase in water absorption with time. However, the rates were different owing to the monomer ratios. Hence the more the hydrophilic groups present, the greater the absorption rate, which shows the characteristics of this poly AN-co-AA grafted hydrogel. Table 2 shows the ratio for different samples [6, 11, 15, 16].

# Effect of MBA with poly AN-co-AA, poly AN-co-NaA, and initiator type

MBA, a crosslinker added as a binding force for comonomers poly AN-co-AA, does not dissolve in water. The samples with different MBA amounts showed the same response with time. The rates of the samples were different, as shown in Figure 5 (a). The poly AN-co-NaA







Fig. 5: (a) MBA effect with NaA (b) MBA effect with AA (c) Effect with different initiator.

Table 2: Sample ratio				
Sample	NaA:AN Ratio			
2	2:1			
1	3:1			
3	4:1			
	AA:AN Ratio			
4	2:1			
5	3:1			
6	4:1			

grafted fabrics were used with different MBA compositions, and the results recorded were not much significant, as shown in Figure 5 (b). The swelling increased with time, showed the hydrophilicity of the grafted hydrogels. Ammonium persulfate and potassium persulfate were the two initiators used in poly AN-co-NaA.

Their effect on water absorbency was observed with time and showed no significant changes, as depicted in Fig. 5 (c). However, the initiator type has no vast effect on the hydrophilic nature of hydrogels [17-19].





Fig. 7: Effect of sodium acrylate composition on ES %, MBA on poly AN-co-AA and poly AN-co-NaA

## Swelling measurement

#### Effect of Acrylic Acid Composition on ES %

Acrylic acid in different proportions was used to prepare poly AN-co-AA. The various compositions showed that with increasing AA amount, the ES % decreased, as shown in Figure 6. Hence this behavior could be because of more hydrophobic groups [14, 20, 21].

# Effect of sodium acrylate composition on ES %, MBA on poly AN-CO-AA and poly AN-CO-NaA

Sodium acrylate at different proportions in poly ANco-NaA was tested. The ES % was seen to be increasing with the compositions, as seen in Fig. 7.

It can be deduced that hydrophilicity increased with greater proportions of sodium acrylate. Fig. 7 shows the effect on swelling showed a decrease in the ES % of the poly AN-co-AA grafted hydrogel. It was majorly due to the cross-linking density increment, which means that the space between copolymer chains was decreased. Hence, the high cross-linking density reduces the water absorption capacity [7, 22]. Here we observe that the ES % rises but



Fig. 8: Acrylonitrile effect on ES % of Poly AN-co-NaA and Poly AN-co-AA

stabilizes after 0.1 g MBA amount as presented in Fig.7. It could be possible because the hydrophilic group is more dominant irrespective of the crosslinker density in the grafted hydrogel. But with later higher proportions, its effect seemed to have significantly changed ES % as it showed significantly less variations. Hence with more cross, linker swelling capacity reduces [21].

## Effect of AN on ES % of poly AN-co-NaA and poly AN-co-AA

The changes of equilibrium swelling were observed on grafted poly AN-co-NaA. Figure 8 shows how drastically the ES % increased with increasing the AN composition. This nature could be due to the more hydrophilic groups present, the higher acrylonitrile (AN) proportion. In Figure 8, it can be vividly depicted that the acrylonitrile (AN) shows a reverse effect on ES % of poly AN-co-AA than the results observed with poly AN-co-NaA. Due to lesser dominancy of a hydrophilic group in poly AN-co-AA shows a decrease in ES % with an increase in AN composition. The hydrophobic groups cause this result.

#### Effect of acrylonitrile with KPS and different Initiator

As the previous observations were done for ammonium persulfate (APS), the initiator was changed to potassium persulphate (KPS), and its effect was recorded. From Figure 9, it was seen that ES % increases with the AN proportion. Hence it is possible to deduce that the initiator type does not influence significantly on the swelling nature of the hydrogel [2, 21]. The initiator type effect was also studied with a constant composition of acrylonitrile of poly AN-co-NaA. The results prove that the influence of the type of initiator is almost negligible. As portrayed from Figure 9, the ES % is moreover the same regardless of the

60



Fig. 9: KPS Effect with Acrylonitrile on ES % and effect of initiator on ES %



Fig. 10. Effect of Ag nanoparticles on ES % of poly AN-CO-NaA and poly AN-CO-AA

initiator used. Cotton fabric was enhanced with APS/KPSactuated graft co-polymerization of poly (NaA- co-AN) and poly (AA-co-AN) copolymers.

# Effect of silver nanoparticles on poly AN-co-NaA and poly AN-co-AA

Silver nanoparticles were embedded onto the hydrogels, as discussed. The effect of silver nitrate composition was observed on ES %, as shown in Figure 10; swelling capacity seemed to have increased with the silver nitrate quantity on ploy AN-co-NaA grafted fabric. Different samples of poly AN-co-AA were embedded with various amounts of silver nitrate. The effects on ES % were observed to be the same as with poly AN-co-NaA. As seen in Figure 10, the increase of Ag nanoparticles increases the swelling capacity of the grafted hydrogel [1, 17].

# Effect of silver nanoparticles on initiator type and acrylonitrile composition

All the samples of poly AN-co-NaA were prepared in



50 1.8 1 1.2 1.4 1.6 2 NaA (grams) Fig. 12. Effect of Ag nanoparticles on ES % the same amount of silver nitrate. The results show that ES

% increase with AN composition due to silver nanoparticles, as shown in Figure 11.

#### Effect of silver nanoparticles on poly AN-co-NaA

When poly AN-co-NaA was observed with and without Ag nanoparticles, the results showed drastic variations, as seen in Figure 12. The increment in ES % for the grafted hydrogel was due to the additional water adsorption in the polymer chains. The embedded nanoparticles increased the pores and free spaces within the network structure of prepared hydrogel, thereby allowing more water holding capacity [15, 16, 18]. Result for poly AN-co-NaA at 1:1 monomer ratio. The ES % with Ag nanoparticles was greater than without Ag nanoparticles.

## Separation efficiency with different oils

Diesel oil and vegetable oil were used selectively at 10% and 20% volume in water. The separation efficiencies for each were observed on different samples, with and without Ag nanoparticles.



Fig. 13: Effect of sodium acrylate on separation efficiency, MBA on the separation efficiency of poly AN-CO-AA and poly AN-CO-NaA for 10% and 20% diesel



------- Effect of Acrylic Acid when 20 % Diesel in Blend Fig. 14: Effect of acrylic acid and acrylonitrile on separation efficiency for 10% and 20% diesel

#### Diesel oil

The oil-water blend of 10:90 and 20:80 (v:v)% was passed over wet poly AN-co-NaA grafted membrane. The water selectively passed through, and oil was retained over the fabric's surface, hence deducing the hydrophilic and oleophobic nature of the gel [6, 8].

# Effect of sodium acrylate on separation efficiency, MBA on separation efficiency of poly AN-co-AA and poly AN-co-NaA

With different proportions of sodium acrylate used in poly AN-co-NaA, the separation efficiency thus improved. As seen from Figure 13, the separation efficiency (SE %) increased with the proportion of sodium acrylate [3, 23]. The effect of sodium acrylate was the same with the 20% oil-water blend [4, 15]. MBA, which was used as a crosslinker, observed the separation efficiency of the grafted hydrogel fabric. From Figure 13, the result shows



Fig. 15: Effect of Acrylonitrile on Separation Efficiency for diesel 10% and 20 %

that SE % decreases. It could be due to crosslinker chains which lessen the spaces between polymer chains, thus causing adequate separation. [4, 18]. Figure 13 shows the same trend of decreasing SE % with increasing MBA proportions. Hence, it is possible to say that crosslinker decreases the working efficiency of the grafted hydrogel if used in greater quantity [12, 20].

### Effect of acrylic acid on separation efficiency

Similarly, the same experiment was performed with the poly AN-co-AA. The separation efficiency increased with the acrylic acid proportion, as shown in Figure 14. Hence, the grafted hydrogel worked better with greater hydrophilicity.

# *Effect of acrylonitrile on the separation efficiency of poly AN-co-AA and poly AN-co-NaA*

Figure 15 shows the changes in the composition of acrylonitrile in poly AN-co-AA were made to observe its effects on SE %. More AN amount decreased the separation because of the lesser hydrophilic groups. Similarly, two different compositions of acrylonitrile (AN) were used, and their effect was observed on the separation. The monomer composition seems to show the same effect with poly AN-co-NaA. It shows that AN composition changes the SE %.

### Effect of initiator type on separation efficiency

Ammonium persulphate and potassium persulphate were employed, and their effect on separation efficiency was observed. Figure 16 shows that the initiator type did not influence the SE %. The percentage decrease is due to the acrylonitrile compositions [4, 7, 21].

### Effect of silver nanoparticles on separation efficiency

The poly AN-co-NaA grafted hydrogel was tested with and without silver nanoparticles. The influence of the



Fig. 16. Effect of initiator type on separation efficiency for 10% and 20% diesel



for 10% and 20% diesel

nanoparticles were recorded to be dominant. As seen in Figure 17, the significant difference between the separation efficiencies of the two bars shows that the silver nanoparticles play a vital role in oil-water blends separation.

#### Vegetable oil

Oil and water blends of 10:90 and 20:80 (v:v)% were prepared similarly to diesel. The composition's effect, type, and without silver nanoparticles were analyzed compared to 10% and 20% of the oil-water mixtures.

# Effect of sodium acrylate composition on separation efficiency, MBA on the separation efficiency of poly AN-co-AA and poly AN-co-NaA

The samples of poly AN-co-NaA with varying amounts of sodium acrylate proportions were prepared and tested. From Figure 18, the SE % seems to be increasing with the increasing amount of NaA. Thereby the presence of hydrophilic-oleophobic groups increases with greater compositions. [3, 6, 20]. The same effects were observed with 20% oil blends. Cross-linker (MBA) added for



Fig. 18: Effect of sodium acrylate composition on separation efficiency, MBA on the separation efficiency of poly AN-co-AA and poly AN-NaA for 10% and 20% vegetable oil



Fig. 19: Effect of acrylic acid on separation efficiency for 10% and 20% vegetable oil

dissolution of the hydrogels in water, create blockchains within the polymer network [15, 18]. The higher concentration of the MBA reduces water permeation, and thereby it is evident from Figure 18 that increasing crosslinker amount reduces oil-water separation. The response of poly AN-co-AA was the same to 10% and 20% oil in the oil-water blend in Figure 18. Different samples of different MBA compositions were tested. Fig. 18 shows that the poly AN-co-NaA samples had the same response to increasing MBA amounts to 10% and 20% oil in the oil-water mixture, respectively [3, 22].

## Effect of acrylic acid on separation efficiency

The as-prepared poly AN-co-AA comprising different amounts of acrylic acid (AA) were observed. When tested for oil-water separation efficiency, they functioned fully, and separation efficiency (SE%) seemed dependent upon AA



Fig. 20: Effect of initiator type on separation efficiency for 10% and 20% vegetable oil



Fig. 21: Effect of acrylonitrile on the separation efficiency of poly AN-co-NaA and poly AN-co-AA for 10% and 20% vegetable oil

composition. As seen in Figure 19, the SE% increased with the AA amount. The grafted fabric showed the same response to 20% oil in the oil-water mixture.

## Effect of initiator type on separation efficiency

As seen in Figure 20 for 10% oil in the oil-water mixture, the SE% is less for the KPS initiator. As for 20% oil in the oil-water mixture, the response is different. The SE% is greater for the KPS initiator.

# Effect of acrylonitrile on separation efficiency of poly AN-co- NaA and poly AN-co- AA

For the acrylonitrile effect, the poly AN-co-NaA grafted fabric efficiency decrease with high AN composition, as shown in Figure 21. The results for 10% oil and 20% oil in the oil-water mixture, respectively, were the same. For poly AN-co-AA grated fabric, the effect of acrylonitrile was analyzed. Figure 21 also shows that the SE% was greater for higher AN concentrations. The responses were the same for both 10% oil and 20% oil in oil-water, respectively.



Fig. 22: Effect of Silver Nanoparticles on Separation Efficiency for 10% and 20% vegetable oil

# Effect of silver nanoparticles on separation efficiency

The oil-water mixtures of 10% oil and 20% oil were tested on poly AN-co-AA and poly AN-co-NaA grafted fabrics. The observations were made with and without embedded silver nanoparticles (Ag NP). From Fig. 22, it is distinct that with silver nanoparticles, the separation efficiency is higher for all the tests performed. [1, 17]. The silver nanoparticles free up spaces and open-pored within the polymer network, increasing water permeation owing to hydrophilic groups. Thus, separation efficiency increases [2, 15, 18].

# Temperature test

At different temperatures, distinct samples were tested to check their oil-water separation and flux, as shown in Figure 23 (a, b). Diesel oil was used, and 8% oil in the oil-water blend was passed each time. The efficiency was seen to be decreasing, and on the other hand, flux is increasing at higher temperatures [4, 15, 18]. It could be because, at high temperatures, oil is less viscous, and some of its molecules could have been mixed within water molecules [9, 16, 19]. This finding agrees with the previously reported work of the author's group on free state swelling of a similar hydrogel system, which suggests that by increasing the solvent temperature, there is a remarkable increase in swelling rate [24]. Oil-water separation efficiency was tested at different temperatures, 30, 45, and 55°C. The mixture was first heated in a water bath to the desired temperature. Then it was set at a hot plate and magnetic stirrer for mixing and temperature measurement. After the desired temperature, the blend was then passed over hydrogel grafted cotton fabric [9, 12, 13, 15].



#### CONCLUSIONS

Cotton fabric was enhanced with APS/KPS- actuated graft co-polymerization of poly (NaA- co-AN) and poly (AA-co-AN) copolymers. With silver nanoparticles, acquired cotton-based hydrogel nanocomposite was then utilized for oil-water division. To upgrade the synthesis of conditions to accomplish the most extreme swelling capacity and subsequently limit separation effectiveness, the impacts of monomers, initiator, crosslinker, and Ag fixation were researched. The temperature effect on separation efficiency was also observed. The most extreme water retentiveness and separation proficiency were accomplished under the ideal states of different copolymers were found to be the following; AA 2.0g NaA 2.0g, AN 1.0 ml, MBA 0.05g, APS 0.075g/KPS 0.06g, and AgNO<sub>3</sub> 40mg. The separation productivity of hydrogels was additionally found to change with monomer type, initiator type, crosslinker sum, presence of Ag nanoparticles, removed oil type, and their volume percentage. In this work, the creation of a novel hydrophilic and submerged oleophobic hydrogel-covered texture was described. It can specifically and successfully separate water from oil-water combinations like diesel and vegetable oil. This water-eliminating hydrogel-covered texture is a decent competitor in mechanical oil-contaminated water treatments and oil slick clean-up. Additionally, producing a novel hydrophilic and underwater oleophobic hydrogel-coated fabric is eco-friendly and environmentally friendly. It has less energy consumption, and it can also be regenerated, henceforth can be reused. This nanocomposite hydrogel is robust to be used under severe acidic conditions.

#### Acknowledgments

The authors would like to acknowledge the Department of Polymer and Petrochemical Engineering

and Department of Chemical Engineering, NED University of Engineering & Technology, Karachi, Pakistan, for supporting this research work.

#### Abbreviation

Acrylontrile	AN
Acrylic acid	AA
Sodium acylate	NaA
Methylene bisacrylamide	MBA
Ammonium persulphate	APS
Silver nitrate	AgNO <sub>3</sub>

Received: Oct. 4, 2021 ; Accepted: Jan. 31, 2022

#### References

- [1] Hu W., Zhang P., Liu X., Yan B., Xiang L., Zhang J., Gong L., Huang J., Cui K., Zhu L., Zeng H., An Amphiphobic Graphene-Based Hydrogel as Oil-Water Separator and Oil Fence Material, *Chemical Engineering Journal*, **353**(1): 708-716 (2018).
- [2] Narayana C., Upadhyay R.K., Chaturvedi R., Sagar R., A Versatile Carbohydrate Based Gelator for the Oil Water Separation, Nanoparticles Synthesis and Dye Removal, New Journal of Chemistry, 41(6): 2261-2267 (2017).
- [3] Fu B., Yang Q., Yang F., Flexible Underwater Oleophobic Cellulose Aerogels for Efficient Oil/Water Separation, ACS Omega, 5(14): 8181-8187 (2020).
- [4] Liu Y., Xia M., Wu L., Pan S., Zhang Y., He B., He P., Physically Cross-Linked Double-Network Hydrogel for High-Performance Oil–Water Separation Mesh, Industrial & Engineering Chemistry Research, 58(47): 21649-21658 (2019).

- [5] Duan C., Liu C., Meng X., Gao K., Lu W., Zhang Y., Dai L., Zhao W., Xiong C., Wang W., Liu Y., Ni Y., Facile Synthesis of Ag Nps@ Mil-100(Fe)/ Guar Gum Hybrid Hydrogel as a Versatile Photocatalyst for Wastewater Remediation: Photocatalytic Degradation, Water/Oil Separation and Bacterial Inactivation, *Carbohydrate Polymers*, 230(1): 1-9 (2020).
- [6] Thakur N., Sharma B., Bishnoi S., Mishra S., Nayak D., Kumar A., Sarma T.K., Multifunctional Inosine Monophosphate Coordinated Metal-Organic Hydrogel: Multi-Stimuli Responsiveness, Self-Healing Properties and Separation of Water from Organic Solvents, ACS Sustainable Chemistry & Engineering, 6(7): 8659-8671 (2018).
- [7] Meng Y., Liu T., Yu S., Cheng Y., Lu J., Wang H., A Lignin-Based Carbon Aerogel Enhanced by Graphene Oxide and Application in Oil/Water Separation, *Fuel*, 278(1): 1-8 (2020).
- [8] Kausar A., Nanocarbon in Polymeric Nanocomposite Hydrogel—Design and Multi-Functional Tendencies, Polymer-Plastics Technology and Materials, 59(14): 1505-1521 (2020).
- [9] Nangia S., Warkar S., Katyal D., A Review on Environmental Applications of Chitosan Biopolymeric Hydrogel Based Composites, *Journal of Macromolecular Science, Part A*, 55(11-12): 747-763 (2019).
- [10] You H., Jin Y., Chen J., Li C., Direct Coating of a Dkgm Hydrogel on Glass Fabric for Multifunctional Oil-Water Separation in Harsh Environments, *Chemical Engineering Journal*, **334(1)**: 2273-2282 (2018).
- [11] Li Y., Zhang H., Ma C., Yin H., Gong L., Duh Y., Feng R., Durable, Cost-Effective and Superhydrophilic Chitosan-Alginate Hydrogel-Coated Mesh for Efficient Oil/Water Separation, *Carbohydrate Polymers*, 226(1): 1-6 (2019).
- [12] Zhu L., Li H., Yin Y., Cui Z., Ma C., Li X., Xue Q., One-Step Synthesis of a Robust and Anti-Oil-Fouling Biomimetic Cactus-Like Hierarchical Architecture for Highly Efficient Oil/Water Separation, *Environmental Science: Nano*, 7(3): 903-911 (2020).
- [13] Li D., Li Q., Bai N., Dong H., Mao D., One-Step Synthesis of Cationic Hydrogel for Efficient Dye Adsorption and Its Second Use for Emulsified Oil Separation, ACS Sustainable Chemistry & Engineering, 5(6): 21649-21658 (2017).
- [14] Fu Q., Duan C., Yan Z., Li Y., Si Y., Liu L., Yu J., Ding B., Nanofiber-Based Hydrogels: Controllable Synthesis and Multifunctional Applications, *Macromol Rapid Commun*, **39(10)**: 1-19 (2018).

- [15] Deng Y., Peng C., Dai M., Lin D., Ali I., Alhewairini S.S., Zheng X., Chen G., Li J., Naz I., Recent Development of Super-Wettable Materials and Their Applications in Oil-Water Separation, *Journal of Cleaner Production*, **266(1)**: 1-26 (2020).
- [16] Liu Y., Yin J., Fu Y., Zhao P., Zhang Y., He B., He P., Underwater Superoleophobic Aptes-Sio<sub>2</sub>/Pva Organohydrogel for Low-Temperature Tolerant, Self-Healing, Recoverable Oil/Water Separation Mesh, Chemical Engineering Journal, 382(1): 1-9 (2020).
- [17] Bhagyaraj S., Krupa I., Alginate-Halloysite Nanocomposite Aerogel: Preparation, Structure, and Oil/Water Separation Applications, *Biomolecules*, **10**(**12**): 1-16 (2020).
- [18] Ghosh T., Das T., Purwar R., Review of Electrospun Hydrogel Nanofiber System: Synthesis, Properties and Applications, *Polymer Engineering & Science*, 61(5): 1-25 (2021).
- [19] Thakur K., Rajhans A., Kandasubramanian B., Starch/Pva Hydrogels for Oil/Water Separation, *Environ Sci Pollut Res Int*, 26(31): 32013-32028 (2019).
- [20] Abdulhussein A.T., Kannarpady G.K., Biris A.S., One-Step Synthesis of a Steel-Polymer Wool for Oil-Water Separation and Absorption, *NPJ Clean Water*, 2(1): 5598-5607 (2019).
- [21] Kordjazi S., Kamyab K., Hemmatinejad N., Super-Hydrophilic/Oleophobic Chitosan/Acrylamide Hydrogel: An Efficient Water/Oil Separation Filter, *Advanced Composites and Hybrid Materials*, **3(2)**: 167-176 (2020).
- [22] Zhu X., Zhu L., Li H., Zhang C., Xue J., Wang R., Qiao X., Xue Q., Enhancing Oil-in-Water Emulsion Separation Performance of Polyvinyl Alcohol Hydrogel Nanofibrous Membrane by Squeezing Coalescence Demulsification, Journal of Membrane Science, 630(1): 1-8 (2021).
- [23] Wang Z., Ma S., Zhong H., Yang W., Pei X., Yu B., Su K., Zhou F., Facile Preparation of Antifouling Hydrogel Architectures for Drag Reduction and Oil/Sea Water Separation, *Materials Today Communications*, 21(1): 1-8 (2019).
- [24] Hashmi S., Nadeem S., Awan Z., Ghani A.A., Synthesis, Applications and Swelling Properties of Poly (Sodium Acrylate-Coacrylamide) based Superabsorbent Hydrogels, *Journal of the Chemical Society of Pakistan*, 41(4): 668-678 (2019).