Hydrogels and Their Novel Applications

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ABSTRACT: *Hydrogels are 3-D (three-dimensional) polymer networks that can be natural or synthetic. After encountering water, do not dissolve but swell. Hydrogels swell in different conditions, such as temperature, pH, and ionic strength, and show other behaviors. Two initiators are used to prepare hydrogels: chemical and radiation initiation. Today, hydrogels have many applications, especially in medical and biomedical science. Vinyl hydrogels are the most applicable ones by worldwide 'polymer chemists'. Allylic monomers cannot be easily polymerized by the free radical polymerization method. The achieved polymers have low molecular weight and cannot convert to hydrogels typically. Inter-penetrating Polymer Network (IPN) hydrogels can be used in the wastewater remediation industry. Amphiphilic and amphoteric semi-(IPN)s are asserted in the metal adsorption and water purification industry.*

KEYWORDS: *Hydrogel; Amphiphilic and amphoteric hydrogel; Vinylic and allylic compound adsorption; Heavy metal adsorption; Wastewater remediation.*

INTRODUCTION

Definition and monomer properties

Hydrogels are *3-D* (three-dimensional) polymer networks that have functional groups [1-3]. Some functional groups include NH_2, SO_2, *C=O*, and *C=O-OH*. Polymers are classified based on the functional groups as electron donor (cationic), electron acceptor (anionic), and neutral polymers. Some of the electron acceptors or anionic polymers include Acrylic Acid (*AA*), Methacrylic Acid (*MAA*), Maleic Anhydride (*MA*), Styrene Carbonic Acid (*SCA*), Styrene Sulfonic Acid (*SSA*), Vinyl Sulfonic Acid (*VSA*), Acryl-Amido-Propane Sulfonic Acid (*AMPS*), and Crotonic Acid (*CA*). Between cationic or electron donor polymers, we can name Allylamine (*AlAm*), Diallyldimethylammonium Chloride (*DADMAC*), Diallyldiethylammonium Chloride (*DADEAC*), Diethylaminoethyl Methacrylate (*DEAEMA*), products of the Aminoethyl Methacrylate, and 4-Vinylpyridine (*VPy*). Neutral polymers include Acrylamide and its derivatives, N-Vinyl-2-Pyrrolidone (*PYy*), Hydroxyalkyl Methacrylate (*HAM*), Hydroxyethyl Acrylate (*HEA*), and hydrophobic acrylates [3-8].

There are two kinds of polymers based on structure: Synthetic and Natural. Chitosan and Sodium Alginate are among the natural polymers, while the other ones referred to above are among synthetic polymers. Synthetic polymers are divided into physical or chemical synthetic hydrogels. Physical, synthetic hydrogels are classified into four groups based on intergroup forces and physical interactions. Ionic hydrogels, hydrophobic hydrogels, hydrogen bonding effect hydrogels, and van der Walls hydrogels. Chemical synthetic hydrogels have covalent bonds. Therefore, they are resistant to modifications [9].

Physical and chemical characteristics

One of the most physical characteristics of hydrogels is swelling after water absorption. [10,11] Swelling properties induce many applications for hydrogels. Polymers

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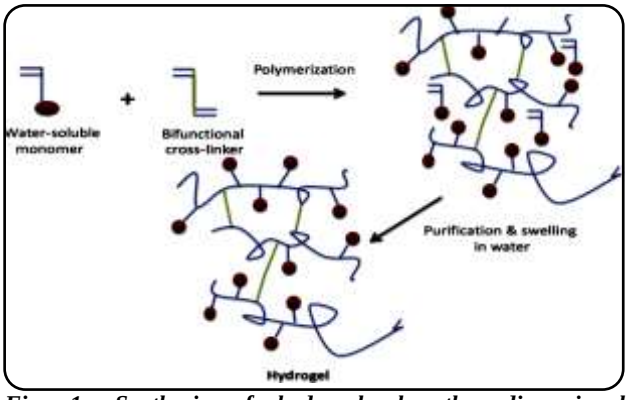

Fig. 1: Synthesis of hydrogels by three-dimensional polymerization [16]

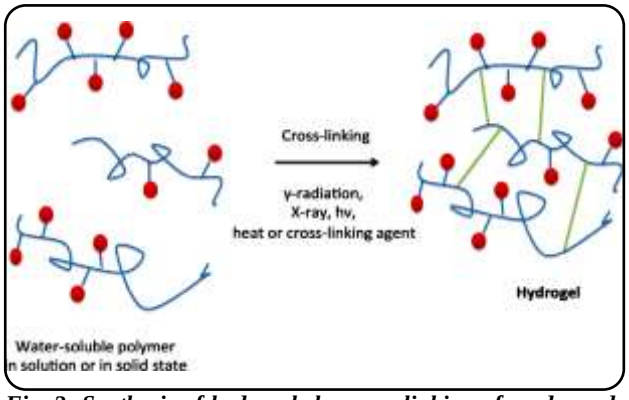

Fig. 2: Synthesis of hydrogels by cross-linking of ready-made water-soluble polymers [16]

need to be prepared to produce hydrogels. Then, many radical centers on polymer chains are activated. Cross-linker agents connect free active radical centers on polymer chains and create hydrogels.

We use two classes of initiators to produce hydrogels: chemical and irradiation. Both initiators can activate free radical centers placed on polymers and hydrogels [12].

In the chemical method of hydrogel synthesis, we use chemical compounds as different initiators (e.g., azo-bis-isobutyronitrile) and cross-linker agents (e.g., N-N'-methylene-bis-acrylamide) (Fig. 1). Hydrogels are prepared by radiation using a *Gamma*-ray, *UV*-ray, and *X*-ray in the irradiation method (Fig. 2) [13-14].

Both chemical and irradiation methods have advantages and disadvantages. Chemical compounds' availability is advantageous, but the high cost and expensiveness of compounds also impurities need different solutions. It costs a lot of time and budget and is among the disadvantages . In the irradiation method, an advantage is reaching high-purity hydrogel and being low-cost. The radiation's low availability and determining the specific radiation dose are disadvantages [14-15].

Structural monomer for hydrogel preparation

Generally, vinyl monomers and allylic monomers were used for hydrogel production in polymer science. Vinyl monomers have been utilized in different applications from 1960 until nowadays. Because they can usually convert to hydrogels through free radical polymerization and low doses of gamma radiation. Some famous vinyl monomers are *AA*, *MA*, *AMPS*, N-iso-propyl acrylamide (*NIPAM*), 2-hydroxymethyl methacrylate (*HMM*), *VPy*, and N, N'-dimethyl acrylamide (*NN'DMA*). Preparing hydrogels from allylic monomers using the free radical polymerization method is complex. Electron transfer from the main chain to the side chain and vice versa occurs during polymerization and hydrogel preparation As a result, two types of polymerization occur along the chain. One is typical polymerization, and the other is degradative chain transfer. These types lead to the conversion by free radical polymerization method and produce low molar mass polymers which cannot produce hydrogels [17].

Allylic polymers cannot produce hydrogel compounds of the low molecular weight of Allylic compounds. However, *AlAm* derivatives have many applications in the industry. Therefore, we must prepare functional polymers by interpenetrating polymer networks (*IPN*) to use polymers with low molecular weight, such as *AlAm* [17].

Hydrogels with different sensitivity to the environment

Hydrogels are capable of swelling or de-swelling reversibly in water. Hydrogels can shrink or expand with changes in external environmental conditions [18]. That means dramatic volume changes occur in response to different physical and chemical conditions. Physical requirements include temperature, electric or magnetic field, light, pressure, and sound. Chemical stimuli have pH, solvent composition, ionic strength, and molecular species (Fig. 3) [18]. Volume collapse or phase transition occurs when the hydrogels' response to stimuli is very prominent [19].

Hydrogel swelling

The equilibrium swelling of hydrogels is calculated from the equation below:

$$Swelling\ ratio = (w_t - w_d)/w_d \quad (1)$$

Where w_t is the weight of the swollen hydrogels at t time,

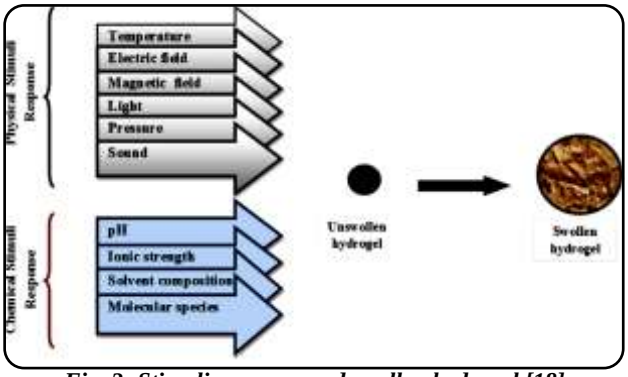

Fig. 3: Stimuli response and swollen hydrogel [18]

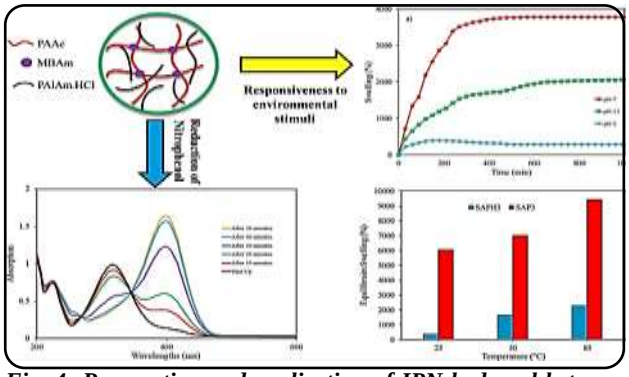

Fig. 4: Preparation and application of IPN hydrogel between acrylic acid and PAlAm [15]

and w_d is the weight of the dried hydrogels. Stimulus-responsive hydrogel, or a biologically sensitive hydrogel, refers to the properties of the hydrogel, including swelling behavior, structure, mechanical strength, or permeability that can change in response to various stimuli [20-25].

Mechanical properties of hydrogels

Chemical hydrogels have more extended stability and good mechanical properties than physical hydrogels. Using toxic cross-linking agents to prepare chemical hydrogels could negatively affect hydrogels' biocompatibility [20,23]. Furthermore, the mechanical properties of hydrogels are an essential parameter applied in medical and tissue engineering [20,24].

Biological properties of hydrogels

The properties of hydrogels in the medical field include biocompatibility and non-toxicity, good mechanical properties, suitable viscosity, stability, and biodegradabil-ity. The hydrogel's mechanical and biological properties have to must same as the tissue that replaces it. [20] *Zhao et al.* achieved optimal mechanical and biological properties by combining cross-linking and electro-spinning methods. They showed that changing the exposure time could change hydrogel's physical and biological properties [23-25]. For example, to mimic actual bone tissue, developing a hydroxyapatite/carbon nanotube / HA CNT composite with suitable mechanical and biological properties is essential instead of bone substitutes [25].

Interpenetrating Polymer Networks (IPN) hydrogel

IPN (Fig. 4) is a complex consisting of polymers with different Maxwell energy levels. Polymers with high Maxwell energy levels are converted to hydrogels, but low energy level polymers cannot convert to hydrogel, and they are retained in the formed hydrogel compound. Therefore, by using *IPN*, we can apply functional groups on the polymer, such as *AlAm*, which cannot convert to the hydrogel [15].

Among important allylic polymers, we can name polyallylamine (*PAlAm*). *PAlAm* has an NH_2 group that makes them more applicable. It mainly has a role in adsorbing sulfates and phosphates in wastewater, [15,17, 26-28]

The thermal resistance of hydrogels was studied using Thermal Gravimetric Analysis (TGA) and Differential Scanning Calorimeter (DSC) in various mole ratios of monomers (1:0.25, 1:1, 0.5:1) in two cases of poly allylamine hydrochloride and poly allylamine (no acid) hydrogels. They found that the thermal resistance of *AlAm* without acid is more than acid form because high-temperature intra-chain, inter-chain, and cyclic reactions happened [17].

Polyelectrolytes

Polyelectrolytes (*PE*)s are polymers that have negative and positive charges. They can transfer many negative and positive charge chains when they are put in the water. [17, 29, 30] To receive more applicable *PEs*, we can encounter them in different pH, temperature, and ionic effect conditions, which show fascinating behavior. Allyamine Hydrochloride (*AlAm.HCl*) is a cationic monomer, and *VSA* is an anionic monomer. *AlAm* and its copolymer with *VSA* are excellent *PE*s that can be used in aqueous systems. *PE*s show complexation by the other polymers having opposite charges. As a tremendous practical point, putting hydrogels in a media containing *PE*s makes them capable of eliminating toxic or heavy metal ions [17, 29,30].

Hydrogels applications

The number of publications on hydrogels since 1960 is over 70,000. However, hydrogel research and

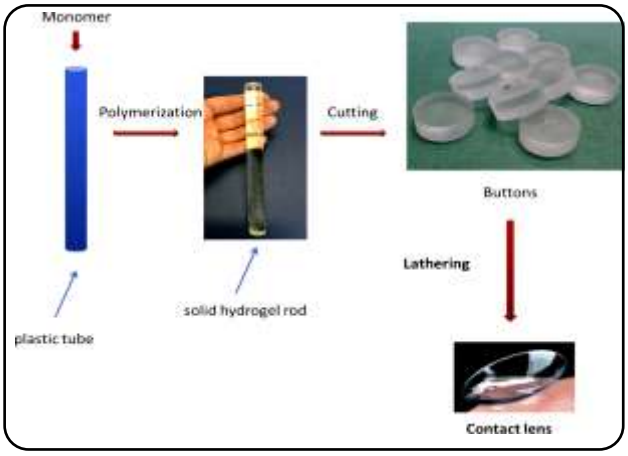

Fig. 5: Scheme of the lathe-cutting technique [16]

development is ongoing, and new application areas are being explored [30-33]. Hydrogels have many applications in different fields. The wastewater remediation [15,31,32] by heavy metals adsorption (sulfates, phosphates, and nitrophenols) [34,35]. They are utilized in the agricultural industry and for medical purposes [34,35]. For example, the preparation of optic lenses stabilization of enzymes [36], and drug delivery are among the other applications of hydrogels in medicine [36,37].

Biomedical applications of hydrogels

Contact lenses

Wichterle et al. used a synthetic biocompatible hydrogel based on poly-2-hydroxyethyl methacrylate (PHEMA) in contact lenses [37]. Lenses were applied first with limited success. In 1965 the National Patent Development Corporation (NPDC) gave the license to that technology. By optimizing Wichterle's spin-casting method, the Food and Drug Administration (FDA) approval for PHEMA lenses was obtained in 1971 [38].

Contact lenses can be prepared based on elasticity as "hard" or "soft." The Hard lenses wear for a longer time, but they could be better bored by wearers and need more time for adaptation. They are primarily made based on hydrophobic polymers, such as poly(methyl methacrylate) (PMMA) or poly(hexa-fluoro-iso-propyl methacrylate) (HFIM). Soft lenses are more flexible and easily tolerable by wearers than Hard lenses. They are made based on hydrogels [39]. A schematic of contact lenses is shown below: (Fig. 5)

Neefe, in the US Patent, described cosmetic hydrogel contact lenses that contain a colored transparent matrix with tiny particles placed in it. Particles reflect light and modify the iris color. Furthermore, hydrogels applied in cosmetic contact lenses correct vision by their elastic characteristic. [40,41] In recently prepared contact lenses, adding selected antimicrobial agents such as 3-(trimethoxysilyl) propyl octadecyl methylammonium chloride to the liquid monomer before polymerization can make lenses with more resistant characteristics to microbial growth [38,42].

Wound dressings

Wounds are a defect in the skin that can occur after injury or trauma. The depth and extent of the skin involvement classify wounds as superficial, partial-thickness, and full-thickness [43]. Effective wound dressings are made in the hydrogels field by considering the effect of every polymer on wound healing processes and patients' primary conditions [43,44]. In the ideal wound dressing industry, making a good absorbent of the excess exudate and toxins, maintaining moisture between wound and dressing, keeping the wound safe from external heat and infections, having good permeability to air, and easy removing without further injury to wound is a goal [45-48].

The most available products are low-adherent dressings, semipermeable films, hydrocolloids, hydrogels, alginates, foam, or antimicrobial dressings [44,49-52].

Drug delivery

Hydrogels are widely used in drug delivery systems because of their physical properties, including water-affinity and adjustable matrix cross-links that give them porous and network structures [53-55]. Hydrogels contain many pores that resulting load and release. When a drug is loaded in a hydrogel, a high concentration of an active substance is maintained in a network for a long time. Then, it can be released controllably by diffusion, swelling, chemical, and environmentally-responsive release mechanisms. Also, preparing sustained-release medicinal products could be possible [53,56]. The diffusion-controlled release systems may be exhibited by the storage or matrix systems. Both permit the drug release by diffusion mechanism through the hydrogel mesh or the filled water pores. A storage delivery system (Fig. 6) contains a drug-maintaining section coated with a hydrogel membrane. The drug-core parts would be capsules, cylinders, spheres, or slabs. The drug concentration is high in the central region, which makes a constant release rate of

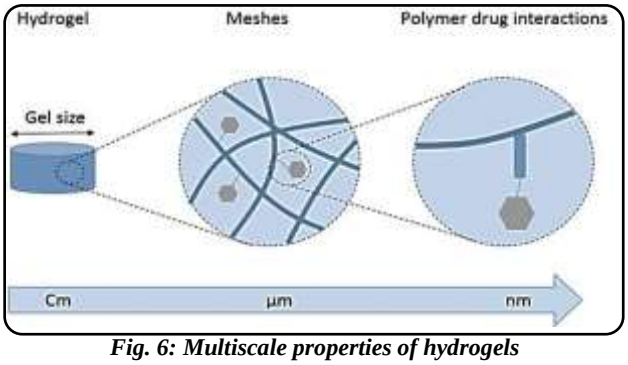

Fig. 6: Multiscale properties of hydrogels

medicine [56]. In the matrix-controlled system, the drug is monotonously dispersed or dissolved throughout the hydrogel network (Fig. 7). Drug release is achieved through the macromolecular mesh or the pores. In this case, the initial release rate is proportional to the square root of time rather than constant and time-independent, as happens in reservoir systems [56]. In swelling-controlled release systems, the medicine is scattered via glassy polymer and begins swelling by contact with a bio-fluid. Then the substance expands and permits the drug diffusion and polymer chains relaxation [56]. The "Case II Transport" process presents constant, time-independent kinetics of substance release. The "Anomalous Transport" is another process that involves combining swelling-controlled release with a diffusion system [57].

The gradient between the medicine loaded in hydrogel and surrounding media allows the diffusion of the active ingredient from the high concentration in the hydrogel into the low concentration media [58].

Considering the application of hydrogels in drug delivery systems, we can refer to the difficulty of insulin injection in diabetic patients. Using complexation gels to load insulin and release adsorbed insulin compounds used by the oral route is among the new horizons in medicinal science [42].

Tissue engineering

Tissue and organ transplantations are among the approved treatments in the medical field. TDonor shortages limit their usage [60-61]. The term "Tissue Engineering" is about the 'structure–function' and the correlation between normal and pathological tissues and the development of biological substitutes for tissue or organ regeneration [62]. It promotes improving or replacing tissues or organs using engineered substances and synthetic processes.

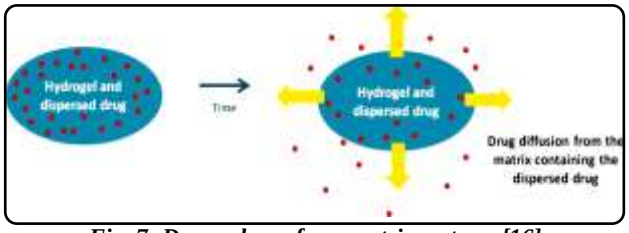

Fig. 7: Drug release from matrix systems [16]

Tissue engineering is the new application area of hydrogels. They are used as filling substances, a transporter for bioactive materials, or as a network that organizes the cells and tissue development (Fig. 8) Space-hydrogels are the most commonly used. They are applied to make bulk, prevent adhesion, and act as biological glue. Medications can be released from hydrogel scaffolds to promote angiogenesis and encapsulate secretory cells. Additionally, they are applied to transplant cells and engineer many tissues, including cartilage, bone, and smooth muscle cells [63].

An essential characteristic of hydrogels is their biocompatibility. That means the ability of the hydrogel to be in contact with the body's organs without harming the tissues [63]. Synthetic substances can form compatible hydrogels for tissue engineering, such as poly(ethylene oxide), poly(vinyl alcohol), poly(acrylic acid), poly(propylene fumarate-co-ethylene glycol), and polypeptides. Agarose, alginate, chitosan, collagen, fibrin, gelatin, and hyaluronic acid are naturally derived polymers used for this purpose [63-64].

Hygiene products

Superabsorbent polymers (SAPs) have been applied in agriculture and diapers for thirty years [65]. SAPs were represented at first by a cross-linked starch-g-polyacrylate [66].

"Superporous hydrogels" (SPHs) are various types of water-absorbent polymers. SPHs are formed by covalently cross-linked hydrophilic polymers form SPHs. Unlike SAPs, they have size-independent rapid swelling kinetics. The first generation of SPHs was prepared by hydrophilic acrylamide, salts of acrylic acid, and sulfopropyl acrylate. In the next generation, SPHs were represented by the "Hydrid SPHs". They can produce an interpenetrating polymeric network by adding a hybrid agent (natural or synthetic water-soluble polymer capable of cross-linking) to the previously made SPH. For example, acrylamide-based SPH is generated by sodium alginate that cross-links between

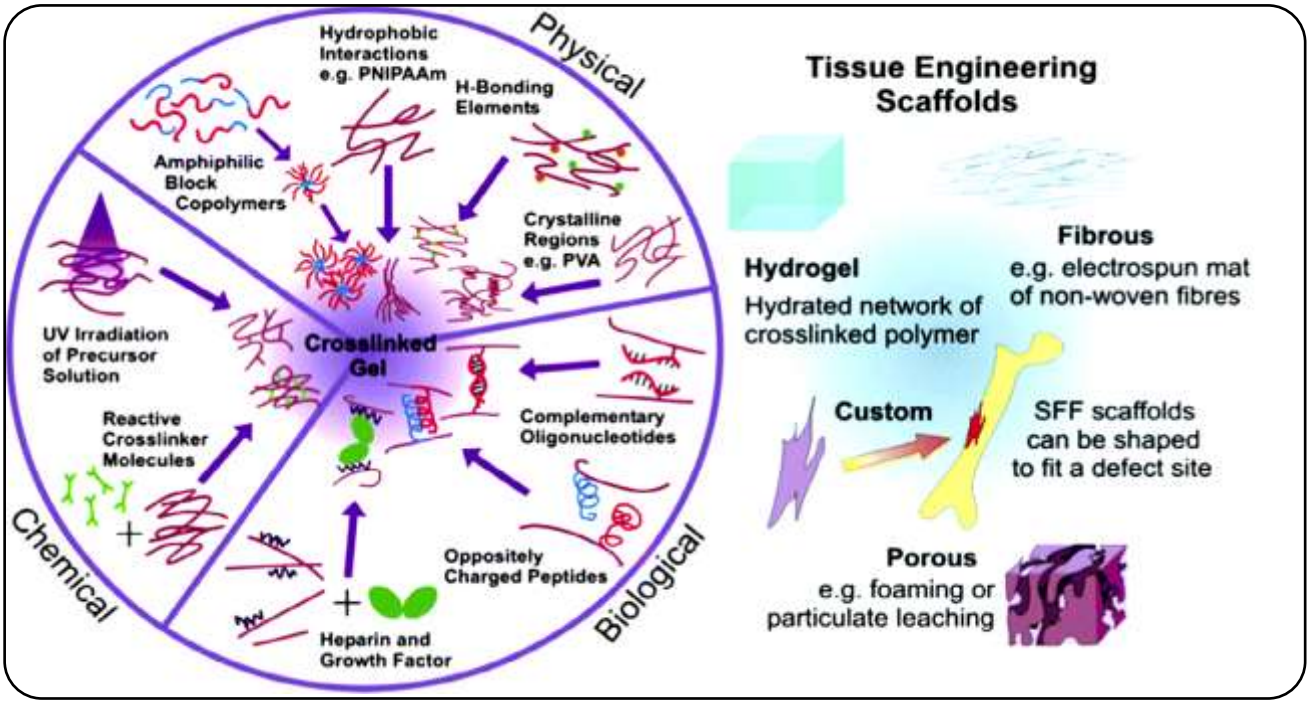

Fig. 8: Hydrogels in tissue engineering (reprinted from E.S. Place, J.H. George, C.K. Williams, M.M. Stevens, Chem. Soc. Rev. 2009, 38, 1139–1151 [64]

alginate chains and calcium ions and forms a hybrid SPH. They have better qualities, such as high mechanical strength and elasticity [65]. Superabsorbent hydrogels, mainly acrylate-based products, are applied in hygiene products to absorb fluids. They hold moisture from the skin, keeping the skin healthy and preventing diaper rash [67-68].

Amphiphilic hydrogels and their applications in wastewater treatment

Amphiphilic hydrogels are a class of hydrogels containing both positive and negative charges in the polymer chains. This characteristic of amphiphilic hydrogels makes them more applicable in industry. In a study, the free radical polymerization method synthesized allylamine hydrochloride-vinyl sulfonic acid (AlAm.HCl/VSA) copolymers in different mole ratios on feed composition 0 *°C* for 50 *h* with a thermal initiator 2,2'-azo-bis(2-methyl-propane diamine) dihydrochloride. The monomer reactivity ratios were calculated by Fineman-Ross (*FR*), Kelen-Tudos (*KT*), Mayo-Lewis (*ML*), and Inverted Fineman-Ross (*iFR*) methods. Investigators conclude that to use allylamine in the hydrogel system, we need to and *IPN*-type hydrogels. Allylamine monomer has a low reactivity ratio, and it is not easy to be polymerized by the free radical polymerization method [30].

In evaluating copolymer, the conversion rate is a second-order reaction. This study described one of the amphiphilic copolymers that are very hard in making hydrogels. It is necessary to use *IPN* hydrogels to resolve the problem. *Sepehrianazar et al*. work on *IPN* hydrogels *AlAm* by radiation to adsorb nitrophenols from wastewater [30].

Jozaghkar et al. prepared *IPN* hydrogels from *PAlAm* to adsorb nitrophenols in wastewater [15]. Because of vinylamine's rare existence, they used *PAlAm*, which is essential and available. *PAlAm* has many applications. In recent years *PAlAm* has been produced using glutaraldehyde and epichlorohydrin as cross-linker agents [17,30].

PAlAm production using gamma radiation in low doses is impossible for the reasons we noted above. *Sepehrianazar et al.* could prepare *IPN* hydrogels from *PAlAm* with a very high of more than 90 *kGy* [35]. Therefore, it is unreasonable to use *gamma* radiation to produce *PAlAm*.

The novel semi-*IPN* hydrogels were synthesized by Polyacrylic acid (*PAAc*)/Polyallylamine (*PAlAm*) and *PAAc*-polyallylamine hydrochloride (*PAH*) with the different molar ratios of components. The optimum amount of cross-linker was found to achieve the maximum swelling degree. *UV–Vis* spectroscopy was utilized to determine the dynamic change of the 4-nitrophenol concentration. (Fig. 1b, c, d) The results revealed the complete absorption

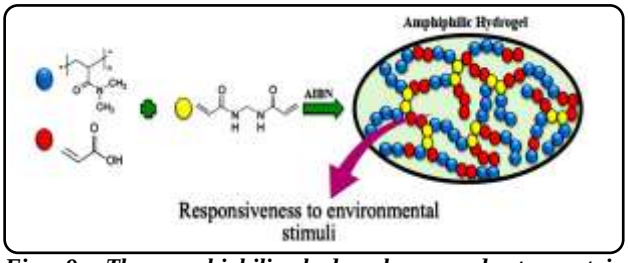

Fig. 9: The amphiphilic hydrogel responds to certain environmental stimuli [67-68]

of the 4-nitrophenol pollutant. They suggest that the prepared semi-*IPN* hydrogel is appropriate for treating wastewater [15].

Fig. 9 presents the amphiphilic hydrogel (one cationic and one anionic). The amphiphilic hydrogels respond to specific environmental stimuli such as N, N'-dimethyl acrylamide/Acrylic acid amphiphilic hydrogels [30].

A study of amphiphilic hydrogels based on different molar ratios of N,N'-dimethyl acrylamide (*DMAM*), and acrylic acid (*AA*) influence on pH, time, temperature, and salinity of the water was investigated. The swelling behavior of hydrogels, kinetic parameters, and swelling diffusion were determined (Fig. 9) [30].

Chitosan is a natural polymer with many functions as an anion and cation adsorbent. It applies to *IPN* hydrogels. In the last years, acrylic acid-chitosan amphiphilic superabsorbent hydrogels have received research interest due to their large amount uptake capacity of water and antibacterial activity. Furthermore, chitosan-acrylic acid hydrogels have an essential role in wastewater treatment. Chitosan has been known as a renewable biopolymer with considerable biocompatibility, biodegradability, and antimicrobial activity [69].

Shin et al. prepared chitosan/*P(AlAm) IPN* and evaluated its swelling rate and other properties [69]. On the other hand, acrylic-chitosan blend hydrogel was prepared with *Gamma*-ray by *Maskawat Marjub et al*. It is a novel polymer that applies in the Cu^{2+} and Pb^{2+}ions adsorption from wastewater. The highest adsorption for Cu^{2+} and Pb^{2+} was 171 and 192 mg/g, se.5 and 5.7, respectively [70].

Today, numerous kinds of hydrogels have been formed. Amphiphilic semi-*IPN* are favored because of their properties. *Maskawat Marjub et al*. used Acrylic acid-chitosan semi-*IPN* hydrogel for Cu^{2+} and Pb^{2+}ions adsorption from wastewater [70]. *Torrado et al.* investigated the drug release behavior of *PAAc*-chitosan hydrogels. In semi-*IPN* hydrogels, each polymer network retains its characteristics, like its homopolymer. When one portion shrinks or swells, another could be created for support via repulsive and attractive interaction of the whole network. These synthesized semi-*IPN* hydrogels are applicable in wastewater remediation, such as removing the nitrophenol derivatives as hazardous waste [71].

One of the other usages of *VSA* is its application in synthesizing poly(N-methylol methacrylamide/*VSA* hydrogels with ^{60}Co-γ ray. It is used in heavy metal ion removal applied in water remediation, absorption, and purification [59a-59b].

One of the other *VSA* applications in hydrogels is the immobilizing enzyme. It catalyzes sucralose and related glycosides in carbohydrates that provide energy sources from plants. It is used widely in the food industry. In this context, Poly (acrylamide/vinyl sulfonic acid) *PA/VSA* and *P*(*AAm)/ PAA* hydrogels were prepared by free radical polymerization in the presence of a cross-linker by *Oztop et al.* It is used as a support for the invertase enzyme. It has thermal and chemical stability with the optimum swelling property comparing its acrylamide hydrogel. Because of the high acidity of *VSA* in water, optimum immobilized enzymes occur in very low pHs [57].

Analysis of the mechanisms of water diffusion in swelling polymeric systems has received considerable attention in recent years because of the critical applications in biomedical, pharmaceutical, environmental, and agricultural engineering fields. Kinetic modeling was conducted based on Fickian diffusion law for the onset stage of swelling to determine the water diffusion into hydrogels (the model is valid only for the first 60% of the swelling):

$$F = \frac{M_t}{M_\infty} = kt^n \qquad (2)$$

Where M_t is the total amount of water intake at time t, M_∞ is the total amount of water intake at an equilibrium state which is determined by a gravimetric method, k is a swelling coefficient which is a parameter correlated with the polymeric network structures, and n is an exponent characteristic of the swelling which represents solvent diffusion modes inside hydrogels. For Fickian kinetics in which the penetrate diffusion is rate limiting, n = 0.5 whereas values of n betweean 0.5and 1 indicate the contribution of non-Fickian processes such as polymer relaxation (Table 1).

Hydrogels are essential in application in biology, the environment, and removing pollutants from water. For this reason, the kinetics of swelling and water diffusion phenomenon into hydrogels should be focused on. First,

Table 1: Values of Diffusion

Diffusion of Gel	Thin membrane	Cylindrical	Spherical
Fickian	0.5	0.45	0.43
Non-Fickian	0.5<n<1	0.45<n<1	0.43<n<1

the rate at which solvent penetrates hydrogel, and second, the relaxation rate of polymer and solvent [72,73].

Hydrogels have various types of capabilities. They respond differently to the various conditions of media. pH, temperature, monomer ratio, and ionic straight are different media conditions. Hydrogels do not swell at low but high pH in the same media with an acidic matrix. In a study in 2022, the maximum swelling rate for acrylamide/allylamine hydrochloride was determined at 80 °*C* in a (1:0.25) mole ratio. They show that the swelling behavior of semi-*IPNs* is attributable to an electrostatic repulsion based on hydrogen bonding between the carboxylic acid groups and an osmotic pressure between freely mobile ions within the gels and ions in buffer solutions. Using *NaCl* and Na_2SO_4 solutions to prepare different ion strengths in concentrations, the maximum swelling (about 1450%) was obtained in a mole ratio of (1:0.25). The kinetic modeling for hydrogel swelling rates manifests that non-Fickian processes, such as polymer relaxation happened. *FT-IR* spectroscopy was used to display the structure of semi-*IPN* hydrogel in different mole ratios, and they found functional groups [30].

Finny *et al.* showed a new custom-made 3D printable eco-friendly hydrogel and fabrication process that produces stable biocompatible adsorbents that can capture and remove heavy metals from aqueous solutions very effectively. The *3D* printable ink contains alginate, gelatin, and polyethyleneimine *(PEI),* which binds heavy metals through primary and secondary amine side chains favoring heavy metal adsorption.These hydrogels are insoluble in water after the metal ion removal, which leads to easy recovery of the tablets. Several benefits are occured with this approach. First, the printing method is scalable. Materials used to formulate the ink are biodegradable and inexpensive. Second, the ink has the metal-binding ability through the *PEI*. These tablets utilize the strong crosslinking properties between *PEI* and metal ions to capture the ions from the media. Third, the hydrogel provides a simple method for removal using tablets. The composition of the tri-polymer *3D* printable ink includes sodium alginate, gelatin, and *PEI*, which together provide an great composite material system for capturing heavy metal ions, easily accessible and environmentally sustainable. Forth, in addition to Cu^{2+} removal, they could be used for removing other heavy metal ions like cadmium, nickel, lead, and cobalt. The tablets and the adsorbent inks can be used for remediation to help treat polluted wastewater, particularly in areas with high heavy metal concentrations [72].

The experimental results showed that the swelling behavior of prepared hydrogels depended on pH, temperature, and ionic strength. The maximum swelling was obtained in pH=7, Temperature =75 °*C*, and *NaCl* and *KCl* concentration of 0.00001 mole. Swellinmoles *KCl* can be attributed to the more ionic radius of K^+ concerning Na^+. The kinetic study manifests a non-Fickian behavior, such as polymer relaxation. The adsorption of Cu^{2+} and Pb^{2+} ions was done by atomic absorption spectroscopy on *AMPS* hydrogels prepared by free radical polymerization [73].

To investigate a large number of hydrogel applications, three monomers (ter monomer) were applied. Ter monomers have many functional groups. *Yetimoglu et al.* prepared N-vinylpyrrolidone/acrylic acid/2-acrylamido-2-methylpropane sulfonic acid-based hydrogel for heavy metal removal from wastewater. The selectivity of the prepared hydrogel was examined for heavy metals adsorption. Its tendency for metal adsorption was different, which was highest for Cd^{2+} than Cu^{2+} and then after Fe^{3+} [74].

In the other study, preparing environmentally sensitive hydrogels (*ESHs*) with specific properties to remove Cu^{2+} from wastewater was performed. *ESHs* were prepared with inter-complex and amphoteric properties by the free radical polymerization method. Two monomers, vinylpyrrolidone (*VP*) and methacrylic acid (*MA*) were prepared while N,N'-methylene-bis-acrylamide was a cross-linker agent [75].

In the Cu^{2+} bindings onto *ESH* experiments, a Langmuir-type (*L*) adsorption was observed regarding the Giles classification system. Binding parameters such as equilibrium constant (K_L), monolayer coverage (Q_m), and maximum fractional occupancy (*FO%*) were calculated as 0.16 $L\ 1/g_{ESH}$, 30 $MgCu^{2+}1/g_{ESH}$, and 81%, respectively. We found a powerful electrostatic effect between the ionic part of *ESH* and cationic Cu^{2+}. These interactions denote removing cationic heavy metals and organic toxic wastes for water treatment. The *VP* units in the *VP-H* and *MA-H* co-hydrogel simultaneously carry positive and negative charges due to keto-enol tautomerism and show amphoteric properties. *UV* spectrometry showed the inter-complex formation between *VP* and *MA* in aqua solution.

A hydrogen bond is formed between the free electron pair in the carbonyl group and the hydroxyl group proton. The structural behavior was investigated by *FT-IR* spectroscopy. Characteristic peaks showed that the critical parameter is the formation of intermolecular hydrogen bonds between the carbonyl group in *VP* and the carboxyl group in *MA*. *TGA* investigated the thermal properties in feed composition's (1:1) mole ratio. The final degradation started at 470 °*C* and continued at 660 °*C*. It can be thought that the disconnection of the remaining main chain, destruction of the entire hydrogel, and carbonization of co-hydrogel. The equilibrium swelling of hydrogels was performed in different concentrations of N,N'-methylene-bis-acrylamide. With the higher cross-linker agent, the swelling percentage is low. Swelling hydrogels were increased in the following order: *VP-H > VP/MA-H > > MA-H*. Diffusion exponents (*n*) are calculated between 0.97 and 0.73. It suggests the non-Fickian type diffusion. The swelling percent in different pH for the *MA-H* shows an inflection point pH=6.4 while *VP-H* shows a peak between 6 and 10. The highest point of the peak was seen at approximately 7.3. After pH= 11, swelling of co-hydrogel decreased due to ring-opening in the *VP* unit. When the temperature is high, the swelling percentage gets high. It was shown for *MA-H*, *VP-H*, and co-hydrogel. A binding isotherm indicates the distribution of adsorbate molecules between the liquid and solid phases when the adsorption process reaches an equilibrium state. Although curves resembling hyperbola generally show Langmurian type in Giles adsorption classification. Freundlich parameters are calculated from the non-linear regression. It obtained Q_m = 30.0321 and *FO%* = 80.8488, and approximately 20% of the binding surface could be filled with cupric ions [75].

CONCLUSIONS

This article briefly and concisely reviews hydrogels and their recent applications in the industry and medicine. Hydrogels are *3-D* compounds that have a functional group on their structure. We referred to the Vinylic and Allylic monomers in preparing hydrogels. Considering the acquired results of the recent studies, Vinylic monomers are the preferred monomers in hydrogel production. Considering hydrogels' practical usage, all three classes of anionic, cationic, and neutral monomers can be applied in hydrogel production. In recent years, using *IPN* and semi-*IPN* hydrogels has been noticed because of difficulties with allylic monomers in hydrogel preparation.

Using amphiphilic hydrogels and *PEs* is a new era in the water remediation industry.

The high cost of Gamma radiation, electron beam irradiation, and X-ray are among the disadvantageous points of some hydrogels. Many applications are attributed to the hydrogels, such as; the agricultural industry, medicine, and wastewater remediation.

Among the newest interests in polymer science, we can name the usage of hydrogels in drug delivery. For example, we can use insulin or neoadjuvant in therapeutic agents to reach better adsorption levels, wide bioavailability, and fewer adverse effects.

In tissue engineering, producing compatible hydrogels with the human body is another new field of hydrogel applications in polymer science.

Recent developments in polymeric materials have led to various hydrogels sensitive to pH, temperature, light, and electric fields, which are used for many applications, especially in the biological and biomedical fields. However, among the hydrogels, those sensitive to pH and temperature were the ones that received the most attention. The use of biocompatible hydrogels could have a promising application in the field of biotechnology.

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