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A Review On Acrlamide Based Hydrogel- Structural Feature,Chemistry, Synthyesis and Its Application

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Abstract*: This paper is a collation and compilation of the research papers in which we tried to review the absorption behavior of acrylamide and its N-substituted derivatives hydrogels for various applications such as heavy metal removal, pharmaceutical, agriculture, controlled drug release etc. They are well-known in foods and medicines, as filters for water purification and as separation materials electrophoresis and proteomic gel. Main emphasis has been laid down on arylamide (AM), methyl methacrylate (MMAtion) and N,N'–methylene–bis–acrylamide (NMBA) hydrogel. Polyacrylamide hydrogel is widely used in Plastic surgery, Watering breads of plants, environmental Medical fields. These hydrogels absorb water to a high equilibrium value, present good biocompatibility and are capable of absorb and release drugs and other compound.*
Keywords: *Hydrogel synthesis, Applications, heavy metal removal, pharmaceutical etc*

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I. INTRODUCTION

In recent year's hydrogels with chelating ligands attracted attention for industrial applications, such as the removal of toxic heavy metal ions from aqueous media, along with other application. Polymeric materials sorbents are effective and economic absorbents for toxic heavy metals in waste water treatments, and it is due to their hydrophilicity, cross linking nature and presence of proper functional groups that are capable for interaction with heavy metal ions. Hydrogels have been widespread applications in the fields of bioengineering, biomedicine, pharmaceutical, veterinary, food industry, agriculture, photographic technology and others. It is used as controlled release systems of drugs, for production of contact lenses and artificial organs in biomedicine, as an adsorbent for removal of some agent in environmental applications, immobilized enzyme kinetics in bioengineering and also as a carrier of water, pesticides fertilizer in agriculture field [1-7].

Hydrogels can be prepared by simultaneous copolymerization and cross-linking of one or more mono-functional and one multifunctional monomer or by cross-linking of a homopolymer or copolymer in solution. Acrylamide and its N-substituted derivatives are widely used for the synthesis of water soluble polymers and hydrophilic gels which find applications in various fields. [8-10].

II. LITERATURE REVIEW

Heavy metal removal from aqueous solution has been traditionally carried out by conventional methods such as chemical precipitation, ion exchange, electrolysis and reverse osmosis.[11,12].However, owing to the operational difficulties and cost of the treatments, attempts have been shown to be an economically feasible alternative method for removing trace metals from waste water and water supplies [13,14].

Thorough survey of the literature reveals that in addition to conventional absorbents like active carbon [15], metal oxides [16,hydrous oxide gels [17],large number of non conventional absorbents have been the removal of metal ions. There adsorbents include fly ash [18] kendu fruits gum dust [19],wood charcoal [20],china clay [21],bituminous coal dust [22],chemically modified saw dust etc [23],lignite coal[24],drums gum dust[25].These absorbents have been found to be cost effective and easily available.

Recently, considerable interest in studying polymer-metal ion complexes has been generated regarding the potential for using polymer systems as a method of treating metal polluted surface waters. Most of the systems employed are resins [26] i.e. cross linked polymer with swelling degree less than 100 percent. In a novel study, Qu rongjun and co-workers[27] synthesized carboxy methyl chitosan/urea formaldehyde snake cage resin and studied the sorption of Cu^{2+},Ni^{2+} and Zn^{2+} ions. The sorption phenomenon was described by Freundlich and Langmuir isotherms. Likewise, Guongling Pei et al[28].synthesized chelating composite membrane with polysulfone and D418 chelating resin ans studied selective adsorption of Cu (II) from aqueous solutions.Similarly,B.L.Rivas and coworkers[29] synthesized crosslinked poly(2acrlamide glycolic acid) resin containing three potential ligand groups and studied adsorption of heavy metal ions like Cu(II),Ni (II) and Cu

(II) from their aqueous solutions both in competitive and non competitive manner.It was possible to remove completely Ni(II) and Pb(II).

In the contest of removal and/or recovery of heavy metal ions from industrial wastewater, most of the above said separation techniques are having one or more drawbacks such as economically expensive, low adsorption capacity, non-selectivity toward heavy metal ions, and other metal ions or production hazardous waste. The use of polymeric matrices for the separation technology is most advisable because of advantages in both economically and technically [30-35].

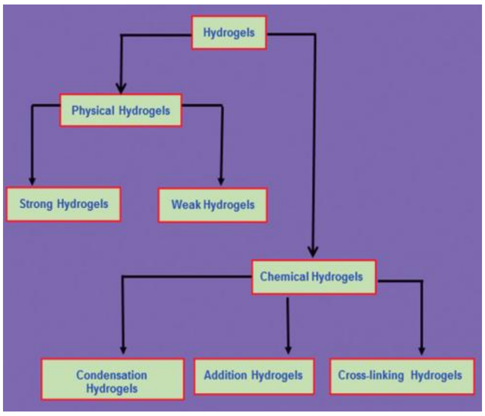
III. HYDROGELS BASED ON ACRYLAMIDE (AM)

Structural features and chemistry of Polyacrylamide

Polyacrylamide (IUPAC poly (2-propenamide) or poly (1-carbamoylethylene) is a polymer (-CH2CHCONH2-) formed from acrylamide subunits that can also be readily cross-linked acrylamide. In the cross-linked form, it is highly water-absorbent, forming a soft gel used in such applications as polyacrylamide gel electrophoresis and in manufacturing softcontact lenses. In the straight-chain form, it is also used as a thickener and suspending agent[36].

The hydrogels are attractive candidates for various biomedical, environmental applications due to their unique biocompatibility, chelating nature, desirable physical and physiological characteristics. They can serve as carriers for drug, protein, and genes and deliver the physiologically important entities in a controlled manner. The tissues scaffolds, which provide structural integrity in tissue engineering applications and environmental remediation of heavy metals and organic dyes [37-40].

Hydrogels can be classified in different ways based on polymeric composition, physical appearance, and type of cross-linking. Schematic representation of this classification is shown in Figure 1



IV. SYNTHESIS OF POLYACRYLAMIDE BASED HYDROGEL

Synthesis of polyacrlamide based hydrogel can be easily done by mainly three method they are Radiation Method, Crosslinking Method, Free radical Polymerization Method,

1. **Radiation Method:** Scientist used these technique for preparation of hydrogels because a polymer in aqueous solution or water-swollen state.[41] Some other group of scientist prepared Acrylamide (AAm)/acrylic acid (AAc) hydrogels,[42] and described that hydrogels have been synthesized from aqueous solutions of acrylamide monomer by gamma radiation[43] Some scientist prepared macroporous, poly (acrylamide) [poly (AAm)] hydrogels by using poly (ethylene glycol) (PEG) polymerization reaction.[44]
2. **Crosslinking Method**: Scientist in 2006 prepared, synthesized apolyacrylamide-based hydrogels by simultaneous polymerization/cross linking.[45-48]
3. **Free radical Polymerization Method**: Several scientists has worked on this method developed a pH sensitive terepolymeric hydrogel system based on acrylamide, methacrylamide, and acrylic acid by free radical polymerization.[49]

Finally it is concluded that hydrogels based on Polyacrylamide is very useful hydrogel which have variety of application in drug delivery, heavy metal removal, medical fields, agricultural fields and industrial fields.

V. HYDROGEL FOR REMOVAL OF TOXIC METAL IONS.

Copolymers having ion-exchange property find applications for removal of heavy metal ions from aqueous solutions.[50–53] Noncompetitive adsorption is used to describe the behavior of metal ion removal from aqueous solution containing only one type of metal. The amount of metal removed by noncompetitive adsorption is about twice of that can be achieved by competitive adsorption. [54] Metal ion chelation polymers, called polychelatogens, contain one or more electron donor atoms such as N, S, O, and P that can form coordinate bonds with most of the toxic heavy metals.[55] Hydrogels containing amide, amine, carboxylic acid, hydroxyl, and ammonium groups can bind metal ions and be good poly-chelatogens for water purification applications[56]

The shortcomings in other separation technologies for the removal of metal ions from dilute aqueous solution led the researchers to explore alternative techniques such as sorption by polymeric hydrogel networks over a long period. The use of hydrogels for the removal of the heavy metal ions from dilute solutions was initiated a decade back. Afterward, various new dimensions have been explored and reported in the field of metal extraction by polymeric networks, beads, and hydrogels [57-64]. Cavus et al. synthesized poly(2-acrylamido-2-methyl-1-propane sulfonic acid-co-itaconic acid) polymers for the removal of Cu(II) and Cd(II) from aqueous solutions. These polymers were shown maximum adsorption capacities 1.685 and 1.722 $mmol.g^{-1}$ for copper and cadmium, respectively. [65]

Ozay et al. [66] developed poly(2-acrylamido-2-methyl-1-propansulfonic acid-co-vinyl imidazole) based magnetic hydrogels for heavy metal ion removal. The maximum uptake capacities obtained were 59.5, 65.8, 83.3, and 88.5 $mg.g^{-1}$ for Fe(II), Cu(II), Cd(II), and Pb(II), respectively. Recently, Luis et al. [67] synthesized super absorbing poly(acrylic acid-co-acrylamide) hydrogels by redox initiator and used for removal of Cu(II) ions from aqueous solutions. These hydrogels achieved maximum uptake capacity of 211.7 $mg.g^{-1}$. Milosavljevic et al. [68] developed poly(acrylamide-co-sodium methacrylate) hydrogels by free radical copolymerization method using poly(ethylene glycol) diacrylate as a cross-linker. They achieved maximum adsorption of 24.05 $mg.g^{-1}$for Cu(II) ions and 32.99 $mg.g^{-1}$ for Cd(II) ions had been obtained at pH 5.0.

Say et al. [69] synthesized poly(hydroxyethyl methacrylate-co-methacrylamidohistidine) beads by the radical suspension polymerization of methacrylamidohistidine and 2-HEMA conducted in an aqueous dispersion medium. The maximum adsorption achieved beads were 122.7 $mg.g^{-1}$ of Cu(II).

Kasgo et al. [70] synthesized nanocomposite hydrogels based on AAm-AMPSNa/clay for heavy metal ion removal. The maximum uptake was observed at pH 3-4.5, and its values were 1.07, 1.28, and 1.03 $mmol.g^{-1}$ for Cu (II), Cd (II), and Pb (II) ion, respectively.

Yetimoglua et al. [71] developed hydrogels by poly(guanidine modified 2-acrylamido-2-methylpropan sulfonic acid/acrylic acid/N-vinylpyrrolidone/2-Hydroxyethyl methacrylate). These hydrogels showed maximum adsorption capacity at pH 5. The maximum uptake capacity of these hydrogels by Langmuir equation was 22.73 $mg.g^{-1}$ and 27.78 $mg.g^{-1}$ for Pb^{2+} and Cd^{2+}, respectively. Doker et al. [72] synthesized poly(N-(hydroxymethyl) methacrylamide-1-allyl-2-thiourea) hydrogels by radiation-induced polymerization for the removal and pre-concentration of Pt(II) and Pd(II).

VI. PHARMACEUTICAL AND AGRICULTURE APPLICATIONS

Urea is an organic compound that is produced by live organisms and also is one of the most important sources of nitrogen for plants, so the study of urea release from hydrogels is useful for both pharmaceutical and agriculture applications Hydrogels Based on Acrylamide, Methyl Methacrylate And N,N'–Methylene–Bis–Acrylamide methacrylate is combined with more hydrophilic monomers in order to improve mechanical properties and for inducing to the polymer the ability to swell in organic liquids [73]The hydrogels that are able to swell in both water and organic are known as amphygels. Methyl methacrylate is a hydrophobic monomer with many applications in polymer industry but of limited use in hydrogels synthesis due to its low water absorption, however MMA has been copolymerized with acrylic acid, methacrylic acid and other monomers in order to produce hydrogels with good mechanical properties.

A series of copolymeric gels of AM, MMA and NMBA as a cross linker agent were prepared by free radical solution copolymerization using a mixture of ethanol and water as a solvent and benzoyl peroxide (BPO) as initiator. Equilibrium water content ($W\omega$) was strongly influenced by copolymer composition. For hydrogels richer in AM, EWC increased as crosslinking decreased. Instead, for high content methacrylate hydrogels, the hydrophilicity of NMBA decreased $W\omega$. Swelling process in distilled water was studied by dynamic swelling measurements (gravimetric method). It was found that synthesized hydrogels fits second–order swelling.[74]

The physical properties of a swollen hydrogel (rubbery consistency, low interfacial tension, and softness) resemble those of natural tissues. In addition they are in general biocompatible, nontoxic, chemically stable and well tolerated when implanted in living beings. All those properties make hydrogels very useful as biomaterials. A hydrogel with high equilibrium water content is in general more permeable and biocompatible. [75]

VII. ROLE OF POLYMERIC MATRICES IN CONTROLLED RELEASE APPLICATIONS

CDRSs are designed to deliver the drugs at programmed rates for predefined periods., CDRSs may be classified into two general ideas: One is targeting and another is controlled release. Systems delivering active agent to the desired tissues and organs are called as “targeted or site specific CDRSs” and systems controlling the release rate of active agent are called as “CDRSs” [76]. Today, polymeric materials still provide the most important parameters for drug delivery research, primarily because of their ease of handling and the ability to readily control their chemical and physical properties via molecular synthesis [77].

The primary aim of CDRSs is to achieve a drug delivery profile that would yield optimum drug levels of the blood serum over a predefined period. CDRDs are designed for sustained as well as long-term administration of drug where the drug level in the blood follows the profile [78], remaining constant, between the desired toxic level and effective level of drug, for an extended period.

5-FU is one of the major drugs used in the treatment of cancer. The treatment of cancer with 5-FU has several shortcomings poor absorption, short biological half-life of the drug (10-20 min in blood plasma) [79]. These limitations may result in suboptimal treatment efficacy or excessive toxicity. Numerous studies have found that controlled release of 5FU in plasma can greatly increase desirable outcomes while minimizing negative side effects of 5FU therapy [80-84]. Hydrogels-based matrices were developed by various polymers for 5-FU release, the nature of polymer; release environment, and release time of hydrogels are presented in Table 3. Mishra et al. [85]

Mishra et al. [86] synthesized pH-sensitive poly(N[-3(dimethylamino)propyl] methacrylamide and 2-hydroxyethyl methacrylate) (PDMAPMA-co-HEMA) hydrogels, and this gels released 88% of 5-FU within 12 h. Liu et al. [87] synthesized a pH responsive colon specific drug delivery system based on starch and poly(aspartic acid) for in vitro 5-FU release. Li et al. [88] developed N-carboxymethyl chitosan-based thermo-sensitive composite hydrogels to deliver an excellent 5-FU releasing effect in addition to the higher drug loading levels. Ibrahim et al. [89] prepared poly(ethylene glycol) grafted carboxymethyl chitosan (CMCs-g-PEG) by photo-induced graft copolymerization method. Giammona et al. [90] developed UV curable copolymeric hydrogels from functionalized glycidyl methacrylate with α,β-Poly(N-2 hydroxyethyl)-DL-aspartamide (PHEA-GMA) and poly(ethylene glycol) dimethacrylate for controlled release application. Garcia et al. [91] prepared PHEMA hydrogels with varying degree of cross-linking and that controls the release of 5-FU. Biswaranjan et al. [92] Eudragit S100 coated Citrus Pectin Nanoparticles (Es-CPNs) were prepared for the colon targeting of 5-FU.

Starch poly(acrylic acid-co-acrylamide) hydrogels have been prepared by physical mixing of the starch and polyacrylonitrile, followed by hydrolysis in the presence ofsodium hydroxide. The hydrogel showed a swelling/shrinking cycle at pH 2 and8, respectively. Poorly water soluble ibuprofen was released from the hydrogel much faster at the intestinal pH than at the gastric pH [93]. Two monomers of methacrylic acid and methacrylamide have been used to prepare hydrogels utilizing a free radical solution polymerization. The hydrogel was intended for oral delivery of an antimalarial drug under physiological conditions. With high loading efficiency of about 98%, the amount of release in simulated gastric (pH 1.2)and colonic environment (pH 7.4) was extensively varied from 29 to 75%respectively[94]. A pH-sensitive hydrogel of hydroxyethyl methacrylate, methacrylic acid and ethylene glycol dimethacrylate was prepared, and its release behavior was examined utilizing a water-soluble drug (ephedrine HCl) and a water insoluble drug (indomethacin)[95].].

VIII. PLASTIC SURGERY

Promising use of hydrogels is bulking agents for treatment of urinary incontinence: smart injectable gels can be involved in clinical procedures where these materials can be used to tighten the urethral channel and reduce patient’s incontinence. With such a simple solution it is possible to erase or at least reduce a consistent social handicap and help patients to hold a normal life [96]. An example of product used in this field is Bulkamid® by Contura International, a polyacrylamide hydrogel is a commercial product developed to help women with incontinence narrowing the conduct.

IX. ELECTROPHORESIS AND PROTEOMICGEL:

Electrophoresis currently represents one of the most standard techniques for protein separation. In addition to the most commonly employed polyacrylamide crosslinked hydrogels acrylamide agarose copolymers have been proposed as promising systems for separation matrices in two-dimensional (2-D)electrophoresis, because of the good resolution of both high and low molecular mass proteins made possible by careful control and optimization of the hydrogel pore structure. Among the materials used for 2-D gel electrophoresis, polyacrylamide crosslinked hydrogels have been extensively investigated in the literature [97].Other polymeric systems alternative to polyacrylamide gels have also been proposed as separation matrices for 2-D electrophoresis including agarose, modified polyacrylamide gels and acrylamide-agarose copolymers [98-99]

X. WATERING BEADS FOR PLANTS:

Another simple application of hydrogels consists in rough powders of polyacrylamide or potassium polyacrylate matrix sold with a huge range of names(Plant-Gel, Super Crystals, Water-Gel Crystals) and used as long term reservoir of water for plant growth in gardening, domestic and sometimes industrial horticulture. On the opposite side as the one of diaper's hydrogel, these materials are optimized for their ability of releasing water, instead of the ability of retaining it. The sustained release of many diverse species is, indeed, one of the main strength of hydrogels on the market, from gardening to genetic engineering. However, even if companies producing such crystals are promoting their practicality and versatility, in the last years the scientific community is questioning about their real utility. As Chalker-Scott from Washington State University pointed out in her publications on the topic, since the commonly used watering crystals are made out of non-renewable materials, whose monomers can be toxic (e.g. acrylamide), the potential risks of their usage are way higher than the benefits of water storage and controlled release that can, in addition, be obtained in many other ways with lower environmental impact [100]

XI. ENVIRONMENTAL APPLICATIONS:

Over past the years, nations gradually started to care about environmental issues and pollution. Many governments decided to opt for greener and safer for the environment policies. Water pollution is one of the biggest issues afflicting especially poor areas of Africa, Asia and South America. Thanks to their affinity for water, hydrogels might be used in two different ways to treatwater source. Hydrogels could be either used like a probe to detect heavy metal ions like in the work by Wang et al. [101]. Moreover, other application of polyacrylamide gels is a flood control device called WATER GEL BAG® and produced by TaiHei Co., Ltd.

XII. MEDICAL FIELDS

A hydrogel for use as a prosthetic device for supplementing, augmenting or replacing cartilage in the intra-articular cavity of a joint and for treatment or prevention of arthritis. The hydrogel may be a polyacrylamide hydrogel obtained by combining acrylamide and methylene bis-acrylamide [102]. He described a bio-stable hydrogel for use in the treatment and prevention of incontinence and vesi couretal reflux.

XIII. CONCLUSION

In this review we provide a historical overview of the developments in hydrogel research from simple networks to smart materials. Hydrogels are widely present in everyday products though their potential has not been fully explored yet. These materials already have a well-established role in heavy metal removal, pharmaceutical, agriculture, controlled drug release Many hydrogel-based drug delivery devices and scaffold shave been designed, studied and in some cases even patented, however not many have reached the market. More progress is expected in thes areas. Limited commercial products with hydrogels in drug delivery and tissue engineering are related to some extent to their high production costs. Swelling and mechanical features of hydrogel polymers have enabled them to find extensive applications in traditional, modern, and novel pharmaceutical area. Desirable hydrogel properties for a given application can be achieved by selecting a proper hydrogel material, crosslinking method, as well as processing techniques. These biocompatible materials are currently used in pharmaceutical dosage forms as super disintegrant, ion exchangeable material, and controlled release platform. Polyacrylamide hydrogel is widely used in Plastic surgery, Watering breads of plants, environmental Medical fields. They are well-known in foods and medicines, as filters for water purification and as separation materials electrophoresis and proteomic gel.

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Dr Nidhi Jain is an Assistant Professor in the area of Applied Sciences (Chemistry) inBharati vidya peeth College of Engineering Lavale, Pune. She achieved her doctoral degree in Chemistry from Govt Model Science College, Rani Durgavati Vishwavidyalaya, Jabalpur (M.P.) Her research topic was "A Study of Ground Water Pollution by Enrichment of Toxic Cations and Anions and its Remedies by Waste Product".

The key focus of the research work was on detection of toxic cations and anions present in the ground water of selected regions of Jabalpur district (M.P.) and to delineate those areas where the ground water was polluted by enrichment of toxic cations and anions. The removal of detected toxic cations and anions by low cost waste product. The main measurement instruments and techniques used in the analysis are Spectrophotometer, Flame Photometer, AAS, pH meter, Conductivity meter, Turbidity meter, Ion meter.

She has published several research papers in reputed international and national journals, conferences and seminars. She has worked on couple of minor project from UGC. She has gained extensive experience not only in the field of academics but also in industry.

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