Water sorption studies and adsorptive features of acrylamide based hydrogels as semi-IPNs and composites

Akrilamid esaslı yarı-IPN ve kompozit hidrojellerin su soğurum çalışmaları ve adsorpsiyon özellikleri

Review Article

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ABSTRACT

In this study, sorption behaviors of water absorbing materials on the basis of acrylamide copolymers as semi-IPNs and composite systems have been investigated. Highly swollen hydrogels made by the polymerization of acrylamide with some hydrophilic co-monomers, some linear polymer and some clays were investigated as a function of composition to find materials with swelling and sorption properties of some metal ions, some pollutant-organics and some dyes. The hydrogels, the semi-IPNs and the composites were prepared by γ-irradiation or free radical solution polymerization in aqueous solutions of monomers and some multifunctional crosslinkers. Swelling experiments were performed in water or other swelling media at 25°C, gravimetrically. For sorption of some metal ions and some dyes into the hydrogels was studied by batch sorption technique at 25°C. This review introduces water sorption studies and adsorptive features of acrylamide based hydrogels as semi-IPNs and composites, synthetic methods, the hydrogel characteristics and their applications.

Key Words
Swelling, hydrogels, acrylamide, semi-IPNs, composites, clay, sorption.

ÖZET

Bu çalışmada, su soğurabilen malzemeler olarak yarı-IPN ve kompozit özellikteki akrilamid esaslı kopolimerlerin soğurum davranışları incelendi. Akrilamidin bazı hidrofilik yardımcı monomerler, bazı doğrusal polimerler ve bazı killerin varlığında polimerleşmeleri ile oluşturulan ve yüksek oranda şişebilen hidrojellerin şişme özellikleri ile metal iyonları, boyar madde ve bazı organikleri soğurum özellikleri kopolimerleri oluşturan maddelerin özelliklerine bağlı olarak araştırıldı. Hidrojeller, yarı-IPN'ler ve kompozitler, ilgili monomerlerin sulu çözeltilerinde serbest radikal polimerleşme tekniği ile ya γ-ışınları ile ya da bazı çok fonksiyonlu çapraz bağlayıcılar kullanılarak elde edilmiştir. Şişme denemeleri suda ya da ilgili şişme ortamında 25°C'da gravimetrik olarak gerçekleştirilmiştir. Metal iyonları ve boyar maddelerin hidrojellere soğurum özellikleri, 25°C'da bir dizi nicel soğurum çalışması değerlendirilerek oluşturulmuştur. Bu derleme, yarı-IPN ve kompozit biçiminde üretilen akrilamid esaslı hidrojellerin, su soğurum çalışmaları, adsorpsiyon yetenekleri, üretim yöntemleri, hidrojel özellikleri ve uygulamaları hakkında bilgiler sunmaktadır.

Anahtar Kelimeler
Şişme, hidrojeller, akrilamid, yarı-IPN'ler, kompozitler, kil, soğurum.

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INTRODUCTION

The use of polymer hydrogels for the removal of heavy metals, dyes and other toxic organics from wastewater or aqueous solutions has been continued to attract considerable attention in recent years [1-10]. Hydrophilic highly swollen crosslinked copolymers called "hydrogels" are synthesized by free radical crosslinking copolymerization with some multifunctional crosslinker with some co-monomers including hydrophilic groups for increasing of their swelling capacity. A hydrogel can be defined as a polymeric material that exhibits the ability to swell in water and retain a significant fraction of water within its structure without dissolving. Small hydrophilic molecules can readily diffuse through hydrogels [1-10].

Crosslinked polymers capable of imbibing large volumes of water have found widespread applications in bioengineering, biomedicine, food industry, water purification and separation process. Although many naturally occurring polymers may be used to produce this type of materials, the structural versatility available in synthetic hydrogels has given them distinctive properties, which in turn have enhanced their practical utility [10-20].

Effective removal of dyes, in connection with wastewater treatment strategy, still remains a major topic of present research. Many methods have been proposed for the removal of dyes, heavy metals and other hazardous materials. Chemical precipitation, membrane extraction, coagulation, complexing, solvent extraction, ion change, and adsorption are some of the commonly used process, but each has its own merits and demerits in its applications. Adsorption or ion exchange using different polymeric materials and synthetic resins is the method of choice in many wastewater treatment processes for removing heavy metal ions, dyes and other hazardous materials from chemical process industries in certain developed countries. Studies have been reported on the use of hydrogels or hydrophilic characteristic crosslinked polymers or copolymers as adsorbents for the removal of dyes, for the recovery of metals, for removal of toxic or radioactive elements from various effluents and for metal preconcentration for environmental sample analysis from aqueous solutions [10-20].

Recently, it was determined that crosslinked polymeric materials having functional groups such as carboxylic acid, amine, hydroxyl and sulfonic acid groups could be used as complexing agents for removal of heavy metals, dyes and hazardous materials from aqueous solutions [10-20]. Acrylamide (AAm) based highly swollen crosslinked copolymers have received much considerable attention for use as "water sor-bent material" at many applications such as purification of wastewater and metal extraction [1,2,7,17-19].

The monomer composition of a copolymer, or semi interpenetrating polymeric networks (IPNs), or composite can be manipulated to influence the permeation and diffusion characteristics of the hydrogel. In this present research, it was of interest to examine the swelling properties and some heavy metal ions or dye sorption capacities of AAm hydrogels with vinyl functional groups containing chemical reagents such as some hydrophilic co-monomers, some synthetic linear polymers and/or some polysaccharides and some clay via free radical solution polymerization method.

Preparation of AAm based hydrogels

AAm based hydrogels are prepared by free radical crosslinking copolymerization of AAm monomer with addition of some hydrophilic co-monomers. For preparation, irradiating with γ-radiation or free radical solution polymerization in aqueous solutions of monomers with some multifunctional crosslinkers has been used. In these studies, used co-monomers are such as itaconic acid (ITA) [21-35], maleic acid (MA) [36-52], crotonic acid (CA) [53-59], tartaric acid (TAR) [60], citraconic acid (CITA) [61], malonic acid (MAL) [62], succinic acid (SUC) [63], citric acid (CIT) [64], mesaconic acid (MESA) [65,66], 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) [67-75], 2-acrylamido-2-methyl-1-propanesulfonic acid sodium salt (AMPSNa) [76-80], 2-hydroxyethyl methacrylate (HEMA) [81], *N*-vinylimidazole (NVI) [82-84], 1-allyl-2-thiourea (ATU) [85-87], acrylic acid (AAc) [88-90], *N*-t-butylacrylamide (TBA)

[91], N-isopropylacrylamide (NIPAM) [92], sodium acrylate (SA) [93-105], sodium methacrylate (SMA) [106-113], potassium methacrylate (KMA) [114], calcium methacrylate (CaMA) [115], 4-styrene sulfonic acid sodium salt (SSS) [1-2]. In these studies, used multifunctional crosslinkers are such as *N,N'*-methylenebisacrylamide (NBisA), ethylene glycol dimethacrylate (EGDMA), trimethylolpropane triacrylate (TMPTA), 1,4 butanediol dimethacrylate (BDMA), poly(ethylene glycol)diacrylate (PEGDA), poly(ethylene glycol) dimethacrylate (PEGDMA), glutaraldehyde (GLU), divinyl benzene (DVB), 1,4 butanediol diacrylate (BDDA) and diallyl phthalate (DP). In these studies, used initiators are such as ammonium persulfate (APS), sodium persulfate (NaPS), azobis(isobutyronitrile) (AIBN) and potassium persulfate (KPS) (Table 1).

Preparation of AAm based hydrogels as semi-IPNs and composite systems.

In these studies, some linear polymers, some polysaccharides and some clay have been used for preparation of semi-IPNs and novel composite systems. Used linear polymers and polysaccharides are such as poly(ethylene glycol) (PEG), poly(vinyl alcohol) (PVA), polyethyleneimine (PEI), gelatin (GEL), poly[(vinylsulfonic acid), sodium salt] (PVSANa), chitosan (CS), bacterial cellulose (BC), starch (STCH), montmorillonite (MMT), attapulgite (ATT), bentonite (BENT) and sepiolite (SEP) (Table 2).

Table 1. Preparative conditions and applications for hydrogels synthesized by solution polymerization method.

Monomer/ co-monomer	crosslinker	İnitiator	Applications (as sorbent)	Refs
AAm/ITA		γ-irradiation	water/dye/UO_2^{2+}, Fe^{3+}, Cu^{2+} nicotine removal, protein sorption	21-29
AAm/ITA	NBisA	APS/TEMED	Water/dye/UO_2^{2+}, Fe^{3+} Cu^{2+}	30-35
AAm/MA		γ-irradiation	water/dye/urea/UO_2^{2+}, Fe^{3+}, Cu^{2+}, nicotine removal, protein sorption	36-35 46,47
AAm/MA	EGDMA, BDMA	APS/TEMED	Water/dye/UO_2^{2+}, Fe^{3+}, Cu^{2+}	48-51
AAm/CA	NBisA, BDMA, EGDMA, TMPTA	γ-irradiation	Water	54-57
AAm/CA	NBisA, BDMA, TMPTA	APS/TEMED	Water	58-59
AAm/TAR		γ-irradiation	Water	60
AAm/CITA	BDMA, EGDMA	APS/TEMED	Water/dye	61
AAm/MAL		γ-irradiation	Water	62
AAm/SUC		γ-irradiation	Water	63
AAm/CIT		γ-irradiation	Water	64
AAm/MES	BDMA, EGDMA	APS/TEMED	Water/dye	65-66
AAm/AMPS	NBisA, EGDMA, BDMA, TMPTA	APS, KPS/TEMED	water/dye/UO_2^{2+}	67-75
AAm/AMPSNa	EGDMA, TMPTA	APS/TEMED	water/dye/UO_2^{2+}	76-79
AAm/HEMA	NBisA	KPS/TEMED	Water	81
AAm/NVI	NBisA, BDMA, TMPTA	APS, NaPS/ TEMED	Water	82-84
AAm/ATU	NBisA	APS/TEMED	Water/ gold removal	85-87
AAm/AAc	NBisA	APS/TEMED	Water	88-90
AAm/TBA	NBisA	APS/TEMED	Water	91
AAm/NIPAM	NBisA	APS/TEMED	Water	92
AAm/SA	NBisA, GLU, DVB	APS/TEMED	Water/dye	93-105
AAm/SMA	NBisA	APS/TEMED	Water/dye/Pb^{2+}	106-113
AAm/KMA	NBisA	APS/TEMED	Water	114
AAm/CaMA	NBisA	APS/TEMED	Water	115
AAm/SSS	NBisA	APS/TEMED	Water/dye	1-2

Table 2. Preparative conditions and applications for hydrogels as semi-IPNs and composites

Monomer/ co-monomer/other materials	crosslinker	İnitiator	Applications (as sorbent)	Refs
AAm/SSS/PEG, Gelatin	PEGDA	APS/TEMED	Water/dye	1-2
AAm/Silica	NBisA	APS/TEMED	Water/dye	3
AAc/AAm/MAc		AIBN	Water	7
AAm/AMPSNa/clay, MMT	NBisA	APS/TEMED	Water/Cu^{2+}, Cd^{2+}, Pb^{2+}	17
AAc/AAm/clay, ATT	NBisA	APS/TEMED	Water/Cu^{2+}, Cd^{2+}, Pb^{2+}	20
AAm/ITA/PEG	NBisA	KPS/TEMED	Water	30
AAm/ITA/PEG	TMPTA	APS/TEMED	Water/dye/ UO_2^{2+}	31,35
AAm/ITA/CS	NBisA	APS	Water	33
AAm/MA/GEL		γ-irradiation	Water	42
AAm/AMPS/PEG	TMPTA, BDMA	APS/TEMED	water/dye	67
AAm/AMPS/BENT	TMPTA, BDMA, EGDMA	APS/TEMED	water/dye/UO_2^{2+}	69,72,75
AAm/NVI/PEG	TMPTA, BDMA	APS/TEMED	Water	82,83
AAm/AAc/PEI	NBisA	APS/TEMED	Water	90
AAm/SA/PVA, GEL, BC	PEGDA	APS/TEMED	Water/dye	93,97
AAm/SA/PVSANa	NBisA	APS/TEMED	Water	96
AAm/SA/PEG	PEGDA, PEGDMA	APS/TEMED	Water/dye	98,99
AAm/SMA/PEG	PEGDMA	APS/TEMED	Water/dye	107,113
AAm/SMA/PVA	NBisA	APS/TEMED	Water	111
AAm/SMA/STCH	NBisA, BDDA, DP	APS/TEMED	Water	112
AAm/clay, SEP	NBisA	APS/TEMED	Water/dye	116

Equilibrium swelling studies

A fundamental relationship exists between the swelling of a polymer in a solvent and the nature of the polymer and the solvent. In dynamic swelling studies, the percentage swelling (S%) of the hydrogels in distilled water was calculated from the related relation. The water intake of initially the hydrogels was followed for a period of time, gravimetrically. Swelling isotherms of the hydrogels were constructed and representative swelling curves of AAm/SA hydrogels are shown in Figure 1 [98]. The swelling increase is due to an increase in the anionic units. The hydrophilic group numbers of AAm/co-monomer based copolymers is higher than those of AAm polymers, and the swelling of AAm/co-monomer based copolymers is greater than that of AAm polymers. When a glassy hydrogel is brought into contact with water, water diffuses into the hydrogel and the network expands resulting in swelling of the hydrogel. Diffusion involves migration of water into pre-existing or dynamically formed spaces between hydrogel chains. Analysis of the mechanisms of water diffusion into swellable polymeric systems has received considerable attention in recent years, because of important applications of swellable polymers in biomedical, pharmaceutical, environmental, and agricultural engineering.

Sorption studies

To observe the sorption of the hydrogels, the samples were placed in aqueous solutions of related solutions and allowed to equilibrate at 25°C. At the end of sorption studies, the hydrogels in related solutions have been shown the color of the related solutions. But AAm hydrogels did not sorb any solute. Spectrophotometric method was applied to the related solutions. The equilibrium concentrations of the related solutions were determined by means of precalibrated scales. Some sorption parameters were determined from the initial and final concentrations of the solutions, calculated from the measured absorbances.

Characterization of the hydrogels

Many techniques which are used for the analysis of the conventional hydrogels can also use for the characterization of semi-IPNs and composites. These techniques are spectroscopic, thermal, mechanical, structural, scanning electron microscopy (SEM) and swelling properties of the typical hydrogels. SEM micrographs of AAm/SMA hydrogel was presented in Figure 2 [106].

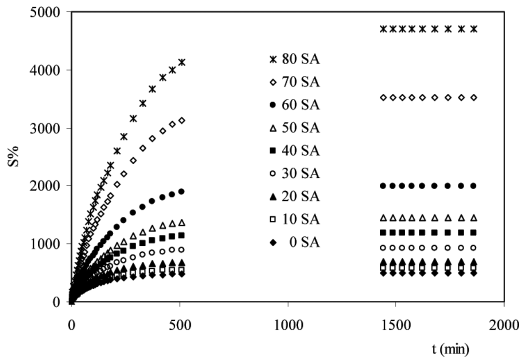

Figure 1. Swelling isotherms of AAm/SA hydrogels [98].

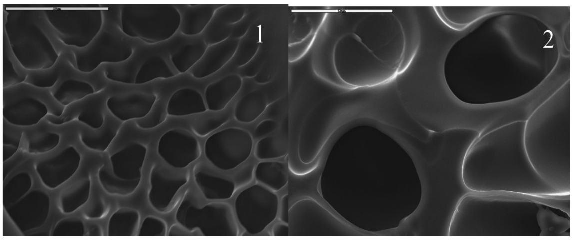

Figure 2. SEM micrographs a) AAm/SMA hydrogel swelled in water (1), pH 2.2 (2) [106].

Applications

Due to their unique properties, the hydrogels, the semi-IPNs and the composites as "water sorbent material" can find applications in different areas at many applications such as purification of wastewater, removal of some dyes, some metal ions and some organic pollutants from aqueous solutions as modeling wastewater. These applications are tabulates in Table 2.

Conclusion

The utilization of these types of hydrogels, in biomedicine, controlled drug delivery, pharmaceuticals, agriculture, biotechnology, environment, sorption, separation, purification, immobilization and enrichment of some species makes hydrogel more popular.

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