PREPARATION AND CHARACTERIZATION OF MAGNETIC NANOPARTICLES IMMOBILIZED IN ACRYLAMIDE BASED HYDROGELS FOR METAL EXTRACTION

SEYED DANIAL NAGHIB

A project report submitted in partial fulfillment of the
requirements for the award of the degree of Master
of Engineering (Chemical)

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TO MY BELOVED FATHER AND MOTHER

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All praises and thanks be to God, who has guided us to this, never could we have found guidance, were it not that God had guided us.

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ABSTRACT

In recent years, smart hydrogel has attracted great attention especially in biomedical and pharmaceutical fields. Hydrogel has polymeric chain structure with a three-dimensional network that is able to swell significantly in aqueous environments. This study involves the development of magnetic hydrogel with nanoparticles for absorption of toxic metal ions (Cu (II), Ni (II), and Co (II)). The nanoparticles with magnetic properties were synthesized in poly acrylamide based hydrogels (method A-C). An in situ preparation process was employed to synthesize the nanoparticles with magnetic properties in hydrogel structure. The differences in rate of absorption between native and magnetic hydrogel was investigated in this study. Compared with native ones, apparently magnetic hydrogels can absorb higher amount of toxic metal ions due to the presence of magnetic nano particles. On the other hand, magnetic nanoparticles also provide large surface area which make them capable of absorbing more toxic metal ions. The highest percentage of absorbtion is attributed to AAm-co-AAc (0.6 gr) while the lowest one is for AAm-co-PEG (0.2 gr) (494 % and 23 % respectively). In absorption of toxic metal ions, AAm-co-AAc (0.6 gr) shows the best performance comparing to other types of hydrogels. This investigation shows that hydrogels and magnetic nano particles are applicable in waste water treatment and metal extraction application. The formation of magnetic nanoparticles in the polymer networks was determined by X-ray Diffraction (XRD), Fourier Transform Infrared (FTIR) spectroscopy and observed using Field Emission Scanning Electron Microscope (FESEM).

ABSTRAK

Dalam tahun-tahun kebelakangan ini, hydrogel pintar telah menarik perhatian yang besar terutama dalam bidang bioperubatan dan farmaseutikal. Hydrogel mempunyai struktur rantaian polimer dengan rangkaian tiga dimensi yang mampu membengkak secara ketara dalam persekitaran berair. Kajian ini melibatkan pembangunan hidrogel magnet dengan nanopartikel untuk penyerapan ion logam toksik (Cu (II), Ni (II), dan Co (II)). Nanopartikel dengan sifat-sifat magnet telah disintesis dalam Hidrogel akrilamida berasaskan poli (kaedah A-C). Satu dalam proses penyediaan situ telah digunakan untuk mensintesis nanopartikel dengan sifat magnet dalam struktur hidrogel. Perbezaan dalam kadar penyerapan antara hydrogel asli dan magnet telah disiasat dalam kajian ini. Berbanding dengan orang-orang asli, apparantly Hydrogel magnet boleh menyerap jumlah yang lebih tinggi ion logam toksik disebabkan oleh kehadiran zarah nano magnet. Sebaliknya, nanopartikel magnet juga menyediakan kawasan permukaan yang besar yang membuat mereka mampu menyerap ion logam yang lebih toksik. Peratusan tertinggi penyerapan adalah disebabkan oleh Aam-co-AAC (0.6 gr) manakala satu terendah adalah untuk AAM-co-PEG (0.2 gr) (494% dan 23% masing-masing). Dalam penyerapan ion logam toksik, AAM-co-AAC (0.6 gr) menunjukkan prestasi terbaik membandingkan dengan lain-lain jenis Hydrogel. Penyiasatan ini menunjukkan bahawa Hidrogel dan zarah nano magnet yang digunakan dalam rawatan air sisa dan logam permohonan pengekstrakan. Pembentukan nanopartikel magnet dalam rangkaian polimer telah ditentukan oleh pembelauan sinar-X (XRD), Fourier (FTIR) spektroskopi dan diperhatikan menggunakan Pelepasan Field Mengimbas Mikroskop Elektron (FESEM).

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LIST OF ABBREVIATIONS

AAm	Acrylamide
AAc	Acrylic acid
AMPS	2-acrylamido-2-methyl-1-propansulfonic acid
AMPS-co-IA	2-acrylamido-2-me thyl-1-propansulfonic acid-co-vinylimidazole
APS	Ammonium Persulfate
DI	Distilled water
DMA	N, N-dimethylacrylamide
FESEM	Field Emission Scanning Electron Microscope
FTIR	Fourier Transform Infrared Spectroscopy
MBA	N, N-methylenebisacrylamide
PAAm	Poly acrylamide
PEG	Polyethylene glycol
PVC	Poly vinyl chloride
SEM	Scanning electron microscopy
TEMED	N, N, N', N'-tetra-methylethylenediamine
XRD	X-ray Diffraction

CHAPTER 1

INTRODUCTION

1.1 Background of Study

In recent years, smart hydrogel has attracted great attention especially in biomedical and pharmaceutical fields. Since the year of 1980s, there is successful demonstration of hydrogel application for cell encapsulation. In the later years, hydrogel has shown its potential application in use as scaffold in tissue engineering, soft contact lenses, wound dressing, implants and controlled release of drug due to its soft tissue biocompatibility.

Hydrogels have polymeric chain structure with a three-dimensional network that are able to swell significantly in aqueous environments without decomposition (Chen *et al.*, 2004). Since hydrogels are soft tissue biocompatible polymers and able to disperse drugs within the network easily with high degree of controlling on release, extensive efforts has been dedicated to use them in pharmaceutical applications (Risbud *et al.*, 2000)

Hydrogels with polyacrylamide family materials have found many uses such as metal extraction and wastewater application. Cross-linked hydrogels able to absorb large amounts of water have found widespread applications in drug delivery, bioengineering, water purification, biomedicine, and food industry (Kim *et al.*, 2003).

Hydrogels have been used in a wide range of environmental, medical, biological and pharmaceutical applications, because of their properties for instants ability of swell in water, biocompatibility, hydrophilicity and lack of toxicity. In recent decades, it was determined that functional groups such as amine, carboxylic acid, sulfonic acid and hydroxyl groups in cross-linked polymeric materials could be used as multifunctional agents for extracting of contaminants from aqueous environments (Kim *et al.*, 2003; Puoci *et al.*, 2008).

Hydrogels can be prepared using natural or synthetic polymers. Table 1.1 shows some of the natural polymers and synthetic monomers/polymers to form hydrogels.

Table 1.1 : Natural and synthetic polymer

Natural polymers	**Synthetic Monomers**	**Synthetic polymers**
Chitosan	Hydroxyethylmethacryate (HEMA)	Polyethylene glycol diacrylate/dimethacrylate (PEGDA/PEGDMA)
Alginate	Acrylic acid (AAc)	Poly acrylamide (PAAm)
Fibrin	Methacrylic acid (MAA)	Polyethylene glycol (PEG)
Collagen	Vinyl acctate (VAc)	Poly acrylic acide (PAAc)

1.2 Problem Statement

It is renowned that toxic metal ions containing Ni(II), Co(II), Cu(II), Hg(II), Pb(II) have many side effects in human and animals health, because they can particularly anchored to small metabolites, and proteins in living organisms prohibitive their actions. In many important industrials, such as waste waters treatment, mining activities, metal plating, petroleum refining, smelting, battery manufacture (Ren *et al.*, 2011; Xiong and Yao, 2009), photographic industries, pesticides, printing and pigment manufacture, toxic metal ions are observed.

Nowdays, many methods and materials have been used as alternative for heavy metal ions removal, such as clay materials, biosorbents, sepiolite, biomass, active carbon and zeolite that must be improved in some section such as their design, separation rate and absorption capacity (Ahmadpour *et al.*, 2009; Barakat and Sahiner, 2008; Naiya *et al.*, 2009). Some disadvantages of these absorbents in the extracting of heavy metal from aqueous environment is that some changes of external factors such as pH, salt, ionic strength, also attendance of other solutes, and temperature of the mentioned media can not be measured (Ju *et al.*, 2009). Hydrogels are considered as smart materials (intelligent materials) because of its remarkable volume alteration in response to the even small alteration in the medium (Yetimoğlu *et al.*, 2007).

In recent decades various type of chitosan and polysaccharide based hydrogels have been used. The above mentioned hydrogels known as an excellent absorbent in wastewater industry, battery manufacturing, due to the fact that the mentioned types of dirty water contain a large quantity of Cu(II), Ni(II), and Co(II) ions (Paulino *et al.*, 2008).

Recently, magnetic absorbents has attracted much attention holding the fact that it has the ability of extracting by applying magnetic field upon extraction of contaminants from aqueous mediums (Zhou *et al.*, 2009). In current research usages and advantages of magnetic hydrogel were investigated. Magnetic hydrogels were used in this work can solve above problems. In addition, magnetic nano particles have been employed in biomedical (Wang *et al.*, 2008), biosensor, and also other relevant field including Nano robots (Sahiner, 2006).

1.3 Research Hypothesis

i. Hydrogels will absorb toxic metal ions.

ii. Magnetic nanoparticles will be synthesized in hydrogels with in situ method.

iii. Hydrogels with magnetic nanoparticles will absorb higher amount of toxic metal ions rather than bare hydrogel.

1.4 Research Objectives

The objectives of the current study are defined as:

i. To synthesize three types of acrylamide hydrogels (poly acrylamide, poly acrylamide co acrylic acid, poly acrylamide co poly ethylene glycol).

ii. To synthesize new three types of magnetic acrylamide hydrogels for metal ion [Cu(II), Ni(II) and Co(II)] extraction applications.

iii. To characterize different structure of magnetic hydrogels.

iv. To compare native hydrogel and magnetic hydrogel in the rate of metal absorption

1.5 Research Scopes

This study was divided into four major scopes:

i. Synthesizing of polyacrylamide hydrogels (poly acrylamide, poly acrylamide co acrylic acid, poly acrylamide co poly ethylene glycol).

ii. In situ synthesizing of Fe_2O_3 and Fe_3O_4 nanoparticles within the hydrogel networks.

iii. Characterization (FTIR, FESEM, XRD) of the formulated hydrogels and studying the physical and chemical properties of gels as well as their microstructure.

iv. Extracting heavy metals (Cu(II), Ni(II) and Co(II)) from water using the developed hydrogels.

1.6 Contribution of the Study

The research suggests using magnetic poly acrylamide blend co-polymered with acrylic acid and polyethylene glycol in order to enhance characteristics of poly acrylamide hydrogels. Extraction of toxic heavy metals from aqueous environments using synthesized hydrogels magnetic nano composites is also aimed. Thermal properties, crystallinity and microstructure of both loaded and unloaded gels are also needed.

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