SYNTHESIS AND CHARACTERIZATION OF POLY (VINYL) ALCOHOL – g - FULVIC ACID HYDROGEL AND ITS APPLICATIONS IN THE REMOVAL OF HEAVY METAL IONS FROM AQUEOUS SOLUTIONS

A Dissertation

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In Partial Fulfillment

of the Requirements for the Degree

Master of Science in Polymer Science and Technology

DECLARATION

I hereby declare that this research project was conducted by me under the supervision of Dr. S. D. M. Chinthaka, Senior Lecturer, Department of Chemistry, University of Sri Jayewardenepura, Sri Lanka. I also certify that this thesis has not been submitted in whole or in part to any University or any other Institute for another Degree/Diploma.

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S. S. P. Perera

2014/07/30

Date

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Dr. S. D. M .Chinthaka

(Supervisor)

Senior Lecturer,

Department of Chemistry,

University of Sri Jayewardenepura,

Sri Lanka.

01/08/2014

Date

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SCHEMES

LIST OF ABBREVATIONS

AAS – Atomic Absorption Spectrophotometer

EDS – Equilibrium Degree of Swelling

FA – Fulvic Acid

-g- - Grafted

IHSS – International Humic Substances Society

LDPE – Low Density Poly Ethylene

PVA – Poly (Vinyl) Alcohol

PVP – Poly Vinyl Pyrollidone

ABSTRACT

Naturally occurring humic substances such as fulvic acid, has a remarkable potential to bind with metal ions. In this study, naturally occurring fulvic acid was extracted from commercially available compost and it was grafted to poly (vinyl) alcohol (PVA) by using Gamma (γ) irradiation to form a hydrogel. The effect of preparation parameters for poly (vinyl) alcohol grafted fulvic acid hydrogels such as fulvic acid concentration in the feed and the irradiation dosage were studied. The produced hydrogels were analyzed by determining the Degree of Grafting (DG), Equilibrium Degree of Swelling (EDS) at different pH values and determining the metal ion adsorption capacity for Cu (II) and Pb (II). Grafting of fulvic acid molecules on to PVA was confirmed by obtaining the FT – IR spectra of grafted hydrogels.

The results of this study shows that EDS increases with increasing FA concentration in the feed and it decreases with the increasing irradiation dosage. It was also observed that, pH of the medium make an intensive impact on EDS of hydrogels. It also shows that both degree of grafting and percentage gelation of hydrogels increase with increased irradiation dosages. The synthesized hydrogels were studied for metal ion binding capacity. Furthermore, synthesized hydrogels show very good capacity of adsorbing Cu (II) and Pb (II) ions from aqueous solutions. It was observed that the hydrogels are more capable of adsorbing Pb (II) ions than Cu (II) ions under studied experimental conditions. Metal ion adsorption capacity for Cu (II) ions is about 68 mg / g and for Pb (II) ions, it is about 75 mg/ g.

CHAPTER 01

INTRODUCTION

1.1. Background

Polymer industry developed, as the population growth created an enormous demand for natural products which cannot be satisfied because of their limited supplies. Today uses of polymer systems are legion and it extends from commodities to aero space applications. Especially various types of novel and tailor made polymers have been using in petroleum industry and also in the biomedical arena for various purposes. Conventional polymers can be modified by using many physical and chemical methods in order to obtain desired properties. Major techniques for the polymer modification are cross linking, composite formation, blending and grafting[1]. From all these techniques, "polymer grafting" is relatively a modern technique which enables to synthesis new polymers or to modify existing polymers. This opens up avenues to set desired physical and chemical properties to the polymer back bone. Grafting has become very versatile, because grafted polymers frequently result in the superposition of properties of both the polymeric backbone and the grafted group.

With the rapid development of the industrial world and due to many human needs, demands for purification systems have increased drastically. Desalination of brackish water, hard water softening, removal of heavy metal ions from aqueous solutions, haemodialysis and waste water treatment are some of the unique applications of the modified polymers. Among all, removal of heavy metal ions from aqueous solutions has become a very important use of modified polymers.

Due to many human activities, various types of pollutants in all environmental matrices are increasing rapidly. As a consequence, heavy metals such as Cd, Pb, Ni, etc. tend to accumulate in natural waters and it has become a serious environmental issue due to their high toxicity and ability to accumulate along food chains. Therefore removal of heavy metals from waste becomes a must requirement in waste water treatment even under low concentrations[2]. To overcome this problem, various traditional and modern purification techniques have been used. Most of the traditional methods such as precipitation of heavy metals as their hydroxides are inefficient and costly. On the other hand, modern techniques such as reverse osmosis and electro dialysis are quite expensive. In order to compromise the effectiveness and the cost, many industries have considered of using modified polymer membranes and hydrogels for purification of industrial effluent.

Surface modified polymers have been used to produce membrane and hydrogels as they give promising solutions for waste water purification. Wide range of modified polymers has been used for this purpose. Synthetic polymers such as Low Density Poly Ethylene (LDPE)[3], poly vinyl alcohol and poly pyrrolidones have been used extensively since 1960. Not only the above mentioned synthetic polymers but also natural and semi – synthetic polymers such as cellulose, chitin, carboxy methyl cellulose (CMC) also have been used for this purpose. In this study PVA was grafted from Fulvic acid which is a naturally occurring humic substance, by using gamma (γ) irradiation.

Polymer chains can be grafted from many types of pendent groups by using various techniques such as chemical enzymatic and irradiation techniques. Since the degree of grafting can be optimized easily by controlling the radiation dosage, irradiation techniques are more efficient and effective and also the clarity of the

modified polymer is remarkably good as it doesn't leave any impurities. Produced hydrogel has very good metal ion adsorption properties under optimum temperature and pH conditions.

1.2. Research objectives

The prime objective of this study is to graft naturally occurring fulvic acid molecules on to PVA backbone by γ-irradiation to obtain a hydrogel which can be used to adsorb heavy metal ions from aqueous solutions. Determining the optimum irradiation dosage and the optimum PVA/FA composition in the feed which gives the best modified polymer with the highest metal ion adsorbing capacity are the secondary objectives of the study. This research also studies the swelling behavior of the hydrogel at different pH values which facilitates the highest equilibrium degree of swelling.

CHAPTER 02

LITERATURE REWIEW

2.1. Polymer hydrogels

With the advancement of science and technology, polymer surface modifications have acquired a great attention. Especially, polymer hydrogels have been used for various exploitations in many sectors such as in electroplating, textile dying and outstandingly for biomedical applications. Polymer hydrogels are three dimensional network structures of polymers which contain significant amount of water (50% - 5000%). Therefore this provides enough free volume for the exchange of ions with the contaminated water. These hydrogels are normally produced either by physical cross-linking which is generally known as a sol – gel transition or by chemical cross linking.

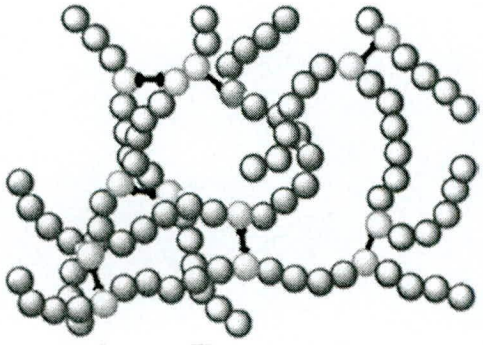

Figure 2.1 –Hydrogel network

Hydrogels which have physical bonds consist of H-bonds, hydrophobic or electrostatic interactions where as chemically cross linked hydrogels are formed by radical polymerization of monomers with the aid of cross linkers, reaction of functional side groups of polymers with themselves or with other purposely added cross linkers, enzymes or high energy radiation. Depending of the nature of the hydrogel network, there are two main classes: namely, permanent hydrogels which have covalently cross