# Removal of Arsenic from Water by Polymeric Materials

**Thesis**
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**Jamia Millia Islamia**

In partial fulfillment of the requirements of the award of the Degree of Doctor of Philosophy in

**Chemistry**

**by**

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Under the supervision of

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# DECLARATION

I, Sadiya Anjum, student of Ph.D. hereby declare that the thesis titled ***"Removal of Arsenic from Water by Polymeric Materials"*** which is submitted by me to the Faculty of Natural Sciences, Jamia Millia Islamia, New Delhi in partial fulfillment of the requirement for the award of the degree of Doctor of Philosophy has not previously formed the basis for the award of any Degree, Diploma Associateship, Fellowship or other similar title or recognition. This is to declare further that I have also fulfilled the requirements of Para 8 (viii and ix) of the Ph.D. Ordinance, the details of which are enclosed at the end of the Thesis.

**Place & Date:**

**Sadiya Anjum**

# CERTIFICATE

On the basis of the declaration submitted by **Sadiya Anjum** student of Ph.D., I here by certify that the thesis title ***“Removal of Arsenic from Water by Polymeric Materials”*** which is submitted to the to the Faculty of Natural Sciences, Jamia Millia Islamia, New Delhi in partial fulfillment of the requirement for the award of the degree of Doctor of Philosophy, is an original contribution with existing knowledge and faithful record of research carried out by her under my guidance and supervision.

To the best of my knowledge this work has not been submitted in part or full for any Degree or Diploma to this University or elsewhere.

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# LIST OF ABBRIVIATIONS

| | |
|---|---|
| PVA | poly(vinyl alcohol) |
| PAA | polyacrylic acid |
| CS | chitosan |
| AA | acrylic acid |
| PVC | polyvinyl chloride |
| TGA | thioglycolic acid |
| TPVA | thiolated PVA |
| STMP | sodium trimeta phosphate |
| GLY | glyoxal |
| BA | boric acid |
| $H_2SO_4$ | sulfuric acid |
| $HNO_3$ | nitric acid |
| HCl | hydrochloric acid |
| NaOH | sodium hydroxide |
| $NaHCO_3$ | sodium bicarbonate |
| $T$g | glass transition temperature |
| $T_m$ | melting point |
| $T_p$ | peak degradation temperature |
| RO | reverse osmosis |
| MF | microfiltration |
| UF | ultrafiltration |
| ΔG | free energy |
| ΔS | entropy term |
| ΔH | enthalpy term |
| T | temperature |
| ºC | degree centigrade |
| IDT | initial decomposition temperature |
| $\Delta H_f$ | heat of fusion |
| $\Delta H_f$(crys) | heat of fusion of 100% crystalline polymer |
| LPR | liquid-phase polymer-based retention |
| BAT | best available techniques |

| | |
|---|---|
| ppb | parts per billion |
| ppm | parts per million |
| w/v | weight by volume |
| v/v | volume by volume |
| mmol/g | milli moles per gram |
| $molL^{-1}$ | mole per litre |
| mg | milli gram |
| g | gram |
| nm | nano meter |
| λmax | maximum wavelength |
| mL | milli litre |
| h | hour |
| min | minutes |
| M | molarity |
| As(III) | arsenite |
| As(V) | arsenate |
| MMAA | monomethyl arsenic acid |
| DMAA | dimethyl arsenic acid |
| SH | thiol |
| OH | hydroxyl |
| 3-D network | 3-dimensional network |
| ATR | Attenuated total reflection |
| BAT | best available technology |
| TDS | total dissolved solid |

# Chapter – 1

# INTRODUCTION
# &
# LITERATURE REVIEW

## 1.1. Introduction

Water has become a highly precious essential resource for all dimensions of life. Over the past few decades, use of water has increased, and in many places water availability is falling to crisis levels. According to the World health organization (2004), more than eighty countries, with forty percent of the world's population, are already facing water shortages and adequate sanitation. In 2000, the United Nations adopted the "*Millennium Development Goals 2015*" part of which has set the goal of reducing the number of people without sustainable access to safe drinking water by half [1]. The costs of water infrastructure have risen dramatically. The quality of water in rivers and underground has deteriorated, due to pollution by waste and contaminants from cities, industry and agriculture. Among them arsenic is considered as a high priority one. At present, among 21 countries in different parts of the world, the USA, Afghanistan, Bangladesh, Cambodia, Canada, Hungary China, Chile, Argentina, India, Japan, Mexico, Mongolia, Myanmar, Nepal, Pakistan, Poland, Taiwan, Thailand, Vietnam have reported high levels of arsenic in part of their groundwater resources [2-5].

Arsenic is a trace metal that ranks 20th in abundance in the Earth's crust and is found associated with igneous and sedimentary rocks [6,7]. It can be easily mobilized in groundwater, depending on pH, redox conditions, temperature, bedrock type, and solution composition. It is a component of more than 200 different minerals, as arsenates, sulfides, arsenides, arsenites, oxides, silicates and elemental arsenic [8]. Several anthropogenic and manmade activities, erosion of rocks, urban wastes, medicinal use, sewage sludge, fertilizers, pigments and other industrial activities contribute to arsenic releases into the environment [9].

Arsenic is a human carcinogen. Consuming drinking water that contains arsenic at high levels has been found to increase the risk of skin cancer and tumours of the bladder, kidneys, liver and lungs [10]. Both long- and short-term exposure to high arsenic levels have their own health implication, e.g., thickening and discoloration of the skin, numbness in the hands and feet, muscular cramping or pain, and other health problems. WHO has set an upper limit for the concentration of arsenic in drinking water at 10 ppb [11]. Different techniques that have been used for the treatment of arsenic contaminated water include co-precipitation, sorption and membrane separation [12]. These techniques have their respective advantages and disadvantages. Among these methods, some are not efficient for arsenite removal because of its complex aqueous chemistry. Since the majority of the people affected worldwide live in small communities, it makes sense to develop a treatment technology tailored for small communities. As a consequence, arsenic is considered highly toxic contaminant and it makes sense to develop tremendous environment friendly and enduring technology for arsenic removal which is tailored for small and under developing communities.

## 1.2. Arsenic

Arsenic is known and used since the history of human civilization. Due to their significant medicinal properties, it has been used as a therapeutic agent for more than 2,400 years [13,14]. In the 15th century, William Withering, who discovered digitalis, was a strong proponent of arsenic-based therapies. He argued,

> ***"Poisons in small doses are the best medicines and the best medicines in too large doses are poisonous"***

The word arsenic is derived from Latin, *arsenicum,* and Greek*, arsenikon,* meaning “yellow orpiment”, identified with *arsenikos,* meaning “male”, from the Greek belief that metals were of different sexes. Arsenic (As, atomic number 33) a steel-gray, brittle, crystalline metalloid appears in Group 15 of the periodic table, below phosphorus and above antimony. It is one of the most widely distributed elements in the earth's crust and in the biosphere [15]. Arsenic ranks 20th in abundance in the Earth's crust, 14th in seawater and 12th in the human body [16]. Arsenic exists in nature in three allotropic forms, α (yellow), β (black), γ (grey), of the metallic state and in a number of ionic forms. Basic chemical and physical properties of arsenic are mentioned in Table 1.1.

**Table 1.1 Chemical and physical properties of arsenic**

| | |
|---|---|
| Atomic Weight | 74.92 |
| Density: | Metal arsenic 5.72 $gcm^{-3}$ at 20 °C,<br>yellow arsenic 2.03 $gcm^{-3}$ |
| Melting point: | 1090 K (817 °C) at 3.7 MPa |
| Sublimation point: | 886 K (613 °C) at 0.1 MPa |
| Electro conductivity | $2.82\times10^{4}$ $Sm^{-1}$ at 0 $^{0}$C |
| Potential of arsenic | with respect to hydrogen gas: 0.24 V |

## 1.3. Arsenic Uses

Arsenic compounds were valued by ancient Indian cultures during the ages of Buddha. The Charaka-Samiti medical test recommended Ala or Haritala (orpiment) and Manashila (realgar) for external and internal medication [17]. Despite this, Fowler's solution[1] used as the medication for a variety of illnesses for 150 years [18]. The demand for elemental arsenic is limited. The main use for metallic arsenic is in the manufacture of nonferrous alloys; high purity arsenic is also used in electronic and semiconductor devices. The following list gives some of the uses of arsenic compounds were shown in Table 1.2.

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[1] *Fowler's solution is 1% potassium arsenite solution discovered in 1976*

**Table 1.2. Uses of arsenic compounds**

| **Field** | **Uses** |
|---|---|
| **Agriculture** | Pesticides, Insecticides, defoliants, wood preservatives, debarking trees, soil erosions |
| **Electronics** | Solar cells, Light emitting diodes (digital watches), optoelectronic devices, semiconductors equipments |
| **Industries** | Glassware electro photography catalysis, anti fouling paints, Dyes and soaps, ceramics, pharmaceuticals farms |
| **Medicines** | Aneamic medicines, Antisphilitic drugs, trypanosomic medicines, amebasis and sleeping sickness. |
| **Metallurgy** | Alloys (automotive body solderand radiators), Battery plates, Hardening agents (i.e. for solding purpose) |
| **Livestock** | Feed additives, cattle and sheep dips, algacides, disease prevention ( swine dysentery) |

## 1.4. Occurrence of Arsenic

Arsenic occurs naturally in rocks, water, soil, air, plants and mammals. It may be released into the environment through a wide variety of activities of natural and anthropogenic origin. Anthropogenic sources of arsenic in the environment include the manufacturing of arsenic based compounds, fertilizers, mining and smelting of arsenic containing ores, waste discharging from industries (e.g., tanneries), combustion of fossil fuels, land filling of industrial wastes, and disposal of chemical warfare agents [19]. Although it has been detected in more than 200 different minerals, the most common are arsenopyrite, orpiment and realgar. In the absence of anthropogenic sources, precipitation contributes little to arsenic levels in groundwater. It can be further released into the environment through natural activities, such as volcanic action, erosion of rocks and forest fires. The occurrence and flow paths of arsenic in the environment are shown in Figure 1.2 [20].

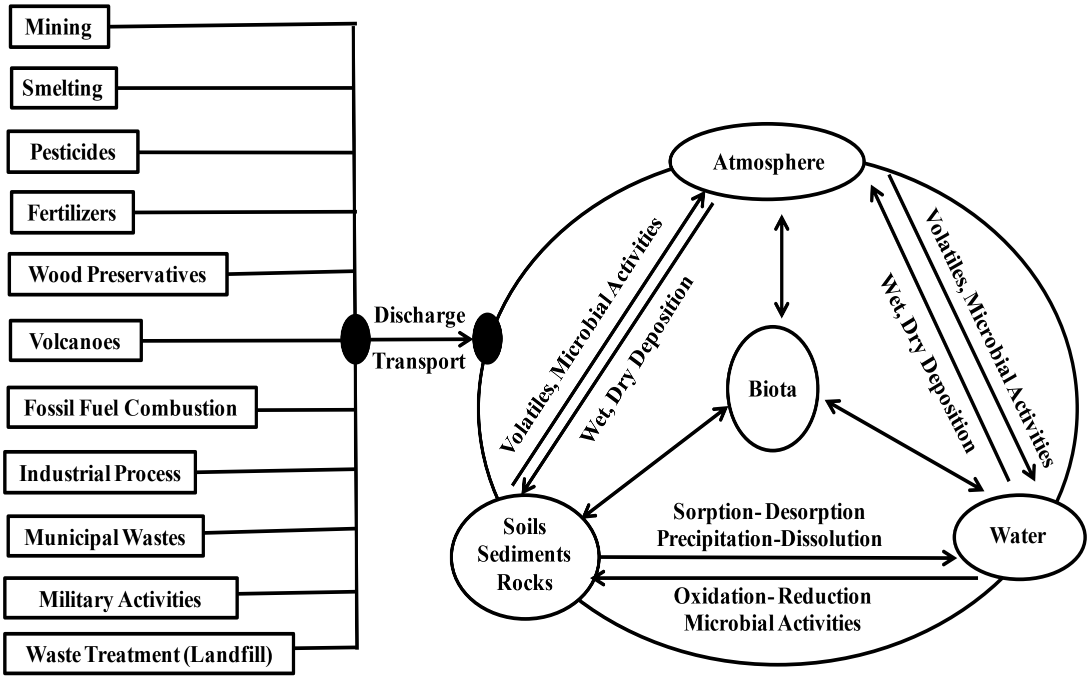

**Fig. 1.1. Arsenic cycle in the environment**

### 1.4.1. Arsenic in Rocks, Minerals and Air

Arsenic occurs in igneous rocks, the greatest concentrations tend to be found in argillaceous sedimentary rocks (e.g. shales and mudstones) and in heavily sulphidic mineralised areas [21]. The SHS[2] found total arsenic concentrations in UK in the range of 0.5 to 143 mg $kg^{-1}$ dry weight for rural soils, with a mean of 10.9 mg $kg^{-1}$ [22]. Arsenic gets into the air from natural and anthropogenic sources. The greatest natural emission source of air arsenic is from active volcanoes, whereas a small amount comes from vegetation and wind-driven dust [23]. The arsenic concentration in air is available from 1 - 10 $ng/m^3$ in rural areas, 0.007 - 1.9 ng/m3 in remote areas and can exceed 1 ppb near emission sources [24].

### 1.4.2. Arsenic in Water

It has been estimated that about one-third of the world's population depends on groundwater for drinking [25]. The level of arsenic in groundwater differs from

---

[2] *The Soil & Herbage Survey is a comprehensive survey of the concentrations of major contaminant in soils & herbage across the UK.*

country to country worldwide. Arsenic occurs in groundwater at typical levels of 0.002-0.01 ppm in the Midwest regions of the U.S.A., New England and greater than 0.01 ppm in other areas in the United States. Mc Neil *et al* analysed data from water treatment utilities (in the United States of America) and reported As(V) levels ranging from 0.021-0.056 ppm, and As(III) levels from 0.0006-0.0014 ppm. Dissolution of arsenic from naturally occurring arsenic-bearing minerals and sediments in India and Bangladesh has put more than 20 million people at risk from drinking arsenic contaminated water.

It is claimed that some 35 million of the population of Bangladesh are subject to arsenic levels in excess of the maximum contaminant level for drinking water as specified by U.S. regulations 10 ppb [27]. Arsenic pollution of groundwater in Ganges River basin, West Bengal, Bihar and Uttar Pradesh, India is known for long. Typical arsenic levels in the groundwater of these areas range from 0.3-0.7 ppm with some waters containing as much as 5 ppm. In India, typical concentration of arsenic in natural waters is; rain water (0.02-16 ppb), river water (<0.02-21,800 ppb), lake water (<0.2-1,000 ppb), estuarine water (0.7-16 ppb), seawater (0.7-3.7 ppb), groundwater (<0.5-50,000 ppb), industrial waters, such as mine drainage (<1-850,000 ppb), oilfield and related brine (230-243,000 ppb) [28-30]. The arsenic concentration reported by Indian Standard drinking water is 0.05 ppm without any relaxation [31]. Chile and Taiwan also experience elevated groundwater levels of arsenic in certain regions [28,29].

### 1.5. Speciation of Arsenic

Speciation of an element may be defined as the analytical activities of identifying and measuring the quantities of one or more individual chemical species that make up the total concentration of the element in a given sample [32]. Some of the challenges include contamination and loss of the species during sample preparation [33]. Arsenic is a metalloid which is present in the environment in four oxidation states, which are denoted -3, 0, +3 and +5. The two main oxidation states of arsenic commonly found in water are +5 and +3 in the forms of arsenate ($AsO_4^{3-}$) and arsenite ($AsO_3^{3-}$) respectively shown in Figure 1.1.

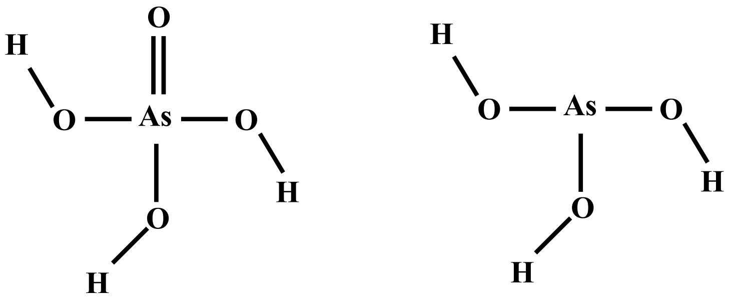

**Fig. 1.2. Molecular structure of arsenate and arsenite**

Arsenate and arsenite are part of the arsenic ($H_3AsO_4$) and arsenous acid ($H_3AsO_3$) systems, respectively. Hence the pH of the system will control the degree of protonation of the acids. In arsenate, the double bond influences its ability to be ionised through the loss of hydrogen ions. The pKa constants (tendency for ionisation) for arsenate and arsenite are as follows [34]:

| | | | | |
|---|---|---|---|---|
| Arsenate: | $H_3AsO_4$ | pK1 = 2.2 | pK2 = 7.0 | pK3 = 11.5 |
| Arsenite: | $H_3AsO_3$ | pK1 = 9.2 | pK2 = 12.1 | pK3 = 13.4 |

At typical pH values (pH 5-8) in natural waters, arsenate exists as an anion while arsenite remains a fully protonated molecule [35]. The rate of oxidation of As(III) to As(V) by dissolved oxygen is slow. The arsenic that is found in natural water is not in the form of simple aqueous arsenic ions, but rather a combination of dissolved forms particulate and colloidal arsenic.

## 1.6. Mobilisation of Arsenic

The unique character of arsenic with respect to its mobilisation as compared to other heavy metalloid oxyanions is its sensitivity to mobilisation over the range of pH found in groundwater (6.5 - 8.5). The mobilisation of arsenic at any given area could be affected by redox condition, pH, biological activity, solid phase precipitation, dissolution reactions, adsorption/desorption reactions, presence of competing anions and [36]. Moreover, the concentration of arsenic can be affected by the interactions between groundwater and rock mass [37]. In summary, the mobilisation of arsenic is very complex.

## 1.7. Arsenic Exposure

The word "Arsenic" is synonymous with poison. The majority of arsenic enters the body in the trivalent inorganic form As(III) *via* a simple diffusion mechanism [38]. Only a small amount of pentavalent inorganic arsenic can cross cell membranes via an energy dependent transport system, after which it is immediately reduced to trivalent arsenic. The largest source of arsenic is usually food, of which the main dietary forms are seafood, rice, mushrooms and poultry [39-42]. Very recently, it has been reported that traditional Chinese herbal products, deliberately fortified with arsenic for therapeutic purposes, may represent a serious health hazard [43]. Colour pigments that are used in the cosmetic industry in the production of eye shadows frequently contain toxic elements, including arsenic [44]. When air containing arsenic dusts is breathed in, the majority of the dust particles settle onto the lining of the lungs [45].

Groundwater contamination by arsenic and other metals has impacted severely on the health of the populations of various regions in the world. Some of the most profound examples of contamination by arsenic occur in Bangladesh and West Bengal, in India, where it has been discovered that almost 43 million people have been drinking water that is laden with arsenic [46,47].

## 1.8. Health effects of arsenic

Arsenic has long been known to cause cancer [48]. Exposure of humans to arsenic is mainly through the consumption of food and water containing high levels of arsenic. The toxicity of arsenical compounds increases from the least toxic organic forms to the most toxic arsine form [49]. The following list gives the order of toxicity of arsenic species:

**Arsine > MMAA > DMAA > As(III) > As(V) > Organic arsenic**

The toxic effects of arsenic depend on its speciation, its solubility and physical form. Arsenate is more readily absorbed than arsenite, and inorganic forms are more readily absorbed than organic forms. Moreover, arsenate is excreted more readily than arsenite and organic arsenic compounds; and organic arsenic compounds are excreted more readily than inorganic forms [50]. Also, bioavailability and toxicity of arsenic can be affected by retention of arsenic species in the body. Elemental arsenic is considered to be of low toxicity on ingestion due to its poor absorption and rapid elimination from the body in an unchanged form [51]. Soluble arsenic compounds are absorbed from the gastrointestinal tract and eliminated as arsenate or organic arsenic through the kidneys [52-54]. Human tissues and fluids contain different arsenic concentrations depending on the level of arsenic intake, the organ investigated and the age of the individual [55,56].

The affinity of As(III) for sulfhydryl groups in enzymes and tissue proteins such as keratin, skin, nail and hair is what makes arsenite more toxic than As(V). As(III) can also denature proteins and enzymes and can damage cells due to increased levels of reactive oxygen species [57-60]. Around 200 enzymes in the body are also inhibited by As(III) [61]. The toxicity of arsenate is due to its structural similarity to phosphate, so that it can substitute for phosphorus in the body [62-63]. In the cell, arsenate is easily hydrolysed which prevents phosphate for being transferred to adenosine diphosphate (ADP) to form adenosine triphosphate (ATP) and as a result depletes the energy of the cell [64]. The most toxic of the arsenicals, arsine causes haemolysis of red blood cells [65,66].

### 1.8.1. Chronic Effects of Arsenic

Arsenic is known to affect variety organisms, including humans [67]. Organs that are associated with the absorption, accumulation and excretion of arsenic species such as the gastrointestinal tract, circulatory system, liver, kidneys, skin and some body tissues are very sensitive to arsenic. Other parts of the body are secondarily affected by arsenic exposure [53]. Signs of chronic arsenic toxicity may include dermal lesions such as, hyperpigmentation, hyperkeratosis, desquamation and loss of hair, peripheral neuropathy, skin cancer and peripheral vascular disease shown in Figure 1.3 [68,69].

These symptoms are observed in populations where arsenic concentrations in the drinking water are high [70]. The skin has a high keratin content which contains several sulfhydryl groups causing it to localise and store arsenic [71]. Ingesting or breathing low levels of inorganic arsenic for a long time can cause darkening of the skin and the appearance of small "corns" or "warts" on the palms and soles shown in Figure 1.3. As a result, skin is highly sensitive to the toxic effects of arsenic. Hypertension and cerebrovascular disease (i.e., cerebral infection) has been linked to long-term arsenic ingestion [72]. Arsenic also decreases DNA repair processes and, as a result, enhances the possibility of cancer, e.g., skin cancer and non-cancer related diseases [73-75].

**Figure 1.3. Chronic affects caused by arsenic in human health dermal lesions, arsenicosis, hyperpigmentation and skin cancer [ref 72,73]**

## 1.9. Arsenic Detection Methods

As mentioned previously, the speciation of arsenic is critically important due to the differences in toxicity of the various species [33]. Since the concentration of arsenic in water is very low, a sensitive (ppb level) and selective method is required for its analysis [76]. There is no standard method reported for determining As(III) and no certified reference materials are available to detect this specie of arsenic from water [77].

The concentration of arsenic in environment can vary depending on factors like the nature of water sample, the type of arsenic in the soil. Therefore precise knowledge of the arsenic compounds present in a system is required for an accurate assessment of the environmental impact of arsenic, which has resulted in an increasing need of analytical method for their determination at micro trace or even ultra trace levels. Many methods have been reported for the determination of different species of arsenic. Inductively coupled plasma with mass spectrometer, also combined with atomic fluorescence spectrometry (AFS), cathodic stripping voltammetry, neutron activation analysis, X-ray fluorescence and colorimetric-solid phase extraction method [78-85].

Some of the reported chromogenic reagents used for the spectrophotometric determination of arsenic are diantipyrylmethane, chlorpromazine, alizarine red S, methyl orange, malachite green, silver diethyl-dithio-carbamate, ammonium pyrrolidine dithio-carbamate, antipyrylazo-4-hydroxybenzenedithiocarboxylic acid and dithiodiantipyrylmethane [86-94]. However most of these methods suffer from large number of limitations such as low sensitivity, need extraction from organic solvents and interference by a large number of ions [86,91].

Comparison of voltammetric and AAS methods for As(III) was used for quantification in presence of iron species in model water samples at very low mineral content [95] A multicommutated flow system based on Hydride Generation Atomic Absorption Spectrometry (HG-AAS) was designed and evaluated for the determination of total arsenic and selenium in water and marine food samples [96,97] Cloud point extraction (CPE) methodology has been employed for the preconcentration of ultra-trace arsenic species in aqueous samples prior to hydride generation atomic absorption spectrometry [98]. The combination of solidification of floating drop microextraction and electrothermal atomic absorption spectrometry were followed for the preconcentration and speciation of arsenic in water specimens [99]. Pervaporation flow injection coupled with AAS was described for the arsenic determination from industrial samples [100].

## 1.10. Arsenic Removal Technologies

Arsenic contamination of groundwater, hastened to a massive epidemic of arsenic poisoning worldwide, has become an important issue and challenge for the world. Arsenic cannot be destroyed, but it can be changed into different forms or it can form insoluble compounds with other elements [101]. At present, the most important challenge for the engineers, scientists and even policy makers is to find an immediate and safe alternative for drinking purpose in areas where drinking water supply contains arsenic. Various treatment technologies have been developed for arsenic removal from drinking water Table 1.3.

**Table 1.3. Comparison of available removal technologies**

| Technologies | Species | Advantages | Disadvantages | References |
|---|---|---|---|---|
| **Oxidation/Precipitation** | | | | |
| Air oxidation<br>Chemical oxidation | As(V) | Relatively simple used *in-situ* arsenic removal.<br>Cost effective, Easy to handle at minority level | Pretreatment required<br>Sludge problem, chemicals required & not feasible at large scale | 102-118 |
| **Coagulation** | | | | |
| Alum coagulation | As(V) | Durable, cost effective, simple & easily available | Pretreatment required & sludge production | 124-142, 181-187 |
| Iron coagulation | | Easily available | Other method required | |
| Lime softening | | Commercially available | Readjustment of pH | |
| Electro coagulation | As(III) | Environment friendly & cost effective | Regeneration is not possible | |
| **Sorption and Ion-exchange Techniques** | | | | |
| Activated alumina | Both Species | Commercially available | Sludge production & low regeneration | 144-156, 157-162, 174-180 |
| Iron coated sand & other adsorbents | | Cheap, no regeneration is required | Maintenance required & sludge production | |
| Ion-exchange resin | | Commercially available, too specific | Disposal issues & less durable | |

| | | | | |
|---|---|---|---|---|
| **Membrane Techniques** | | | | |
| Nanofiltration | Both Species | Commercially available | Expensive and high water rejection | 101,149,169-171, 188-190 |
| Reverse Osmosis | | Commercially available & no sludge production | High tech operation and maintenance | |
| Micro and Ultra Filtration | | No sludge production | Membrane fouling | |
| Electrodialysis | | Commercially available | Specific for As(V) | |
| **Biological Methods** | | | | |
| Phytoremediation | Both Species | Economic and acceptable | Not fully developed | 192-209 |
| Bioremediation | | Commercially available & cost effective | Difficult to operate | |
| Phytofiltration | | Promising technology | Not efficient in temperate zone. | |
| **Commercial Scale Techniques** | | | | |
| Solvent Extraction | As(V) | Easily handle | Not fully developed | 5,101,104, 165 |
| Buckets Unit | | Commercially available | Requires chemicals & Needs periodical change | |
| Read F unit | | No pretreatment & high selectivity | Costly & not efficient for rural areas. | |
| **Indigenous Filters** | | | | |
| Sono 3-Kolshi Filter | Both Species | Easy technique | Use & through unit | 154,155, 165-167 |
| Granet Home-made Filter | | No chemical required | Inadequate quantity of water required | |
| Shafi-Adarsh Filter | | Good removal capacity | Quickly clogged filter media | |
| **Cartridge Filters** | | | | |
| Chiyoda Unit, Japan | Both Species | Easy to handle | Expensive technique | 154,155,166 |
| Coolmart Purifier, Korea. | | Cost effective & easily operate. | Contamination problem | |
| Traditional Sand Filters | | Remove pathogens, cheap & easily available. | Rusting problem | |
| House hold AIIH&PH Plant | | Modern method | It's required periodic sludge cleaning. | |
| **Polymeric Materials** | | | | |
| Natural Polymers | Both Species | Easily available & used in rural areas | Not fully developed | 210-233 |
| Synthetic Polymers | | Efficient, cost effective technique & regeneration ability | Required advance treatments & instruments | |

Most of them are applicable at a commercial level while the rest are used in a minor scale. The commonly used technologies are classified as conventional and emergent technologies.

### 1.10.1. Conventional Technologies

The most common technologies include processes that can be used alone or in combination, such as oxidation, co-precipitation and adsorption onto coagulated flocs, lime treatment, adsorptions, ion exchange resins and membrane technologies. Most of them are well understood technologies for arsenic removal in large and medium scale treatment plants for centralized services.

#### 1.10.1.1. Oxidation and Reduction

Oxidation is a previously required step to transform As(III) species in more easily removable As(V) species. Simple direct aeration is slow, but a number of chemicals, including gaseous chlorine, hypochlorite, ozone, permanganate, hydrogen peroxide, manganese oxides and Fenton's reagent ($H_2O_2/Fe^{2+}$) can be employed to accelerate oxidation [102-105]. Several author reported that, hydrogen peroxide is a strong oxidizing agent and can contribute to the oxidation of As(III) at suitable conditions [106-108]. Numerous authors have also described removal of arsenic by chemical oxidation and sorption onto metal oxides [109-112]. Solrini *et al* investigated the efficiency of the oxidation of As(III) by means of four conventional oxidants (chlorine dioxide, sodium hypochlorite, potassium permanganate and monochloramine) with different test conditions [113].

In-situ oxidation of arsenic and iron in the aquifer has been tried under DPHE Danida Arsenic Mitigation Pilot Project [114]. Hug *et al* studied the solar oxidation process to remove arsenic from drinking water in Bangladesh [115]. Ultraviolet radiation can be used to catalyze the process of oxidation of As(III) in presence of other oxidants like oxygen [116]. Dodd *et al* also studied kinetics and mechanistic aspects of As(III) oxidation by aqueous chlorine, chloramines and ozone and its relevance to drinking water treatment [117]. Katsoyiannis *et al* have applied biological iron and manganese oxidation to remove As(III) and As(V) from groundwater without the use of chemical oxidizing agents, apart from oxygen and bacteria [118].

#### 1.10.1.2. Precipitation

Precipitation has been the most frequently used method to treat arsenic contaminated water in numerous pilot- and full scale applications. This techniques has an advantage over other methods due to the insolubility of certain arsenical inorganic compounds such as As(III) sulfide, calcium arsenate and ferric arsenate may be proposed to remove As from water [119]. Arsenic may be converted to an insoluble form by precipitation, co-precipitation onto the hydroxide phase, or adsorption onto a solid oxyhydroxide surface site [120,121]. However, the method is generally not suitable because of the instability of most of the solids, also inadequate for direct disposal [119]. The removal of arsenate from contaminated water sample by precipitating arsenate with calcium phosphate hydroxyapatite was studied under conditions that induce arsenate incorporated calcium phosphate hydroxyapatite [122]. Brunet *et al* investigated the precipitation of As(III) sulphide in sulphate-reducing conditions for removal of arsenic in a waste product [123].

#### 1.10.1.3. Coagulation-Filtration

Coagulation–filtration is the most common technology for arsenic removal. Arsenic is removed in the pentavalent form, which adsorbs onto coagulated flocs and can be then removed by filtration. As(III) has to be previously oxidized, generally with chlorine [124]. The most used coagulants are aluminum sulfate $Al_2(SO_4)_3$, iron chloride ($FeCl_3$) and ferrous sulfate ($FeSO_4$), iron salts being generally better removal agents. $FeCl_3$ generates relatively large flocs, while smaller ones are formed with $FeSO_4$ [125-128]. The As(V) removal efficiency of preformed $Al_{13}$ was compared with that of in situ formed $Al_{13}$ considering various Al dosages and pH values [129]. Iron salts were more effective at removing arsenite than aluminum salts. This may be due to some of the aluminum remaining soluble, and passing through filtration steps, while iron salts completely form particulate iron hydroxide [130-132]. Liu *et al* investigated the effectiveness and mechanism of permanganate enhancing As(III) co-precipitation with ferric chloride [133]. Yuan *et al* adopted the ferrate as coagulation and evaluated the performance of ferrate for arsenic removal by experiment [134].

Filtration is a necessary step. Using a 0.1 or 1.0 mm filter, arsenate removal improves to more than 96% [135-137]. The coagulation–filtration technology only uses common chemicals, installation costs are small and it can be easily applied to large water volumes. The technology proved to achieve 80–90% of As removal [138-141]. Chang *et al* stated the treatment unit packed by granular adsorbent of Fe-Mn binary oxide incorporated into diatomite for arsenic removal from anaerobic groundwater without any pre-treatment or post-treatment [142]. Later, various small and medium plants have been successfully implemented in the country with this methodology.

#### 1.10.1.4. Lime Softening

Lime softening technology is used in the presence of water and carbonic acid to remove arsenic and the process ending with a coagulation step. The method is able to treat water with high hardness, especially at pH above to 10.5. Slaked lime and soda ash are added to precipitate unwanted polyvalent metallic ions. Arsenic removal may be facilitated by calcium carbonate, magnesium hydroxide, and iron hydroxide and to a lesser extent manganese hydroxide precipitates. Removal rates may be increased significantly by adding some iron to influent [143]. The main disadvantage is a very high pH in the resulting water, which implies a further acidification step. On the other hand, a very high dose of coagulant is needed and relatively low removal efficiencies. However, secondary treatments are being required [5,104,124,126,135].

#### 1.10.1.5. Adsorption

Adsorption technology has been widely used to treat ground water containing arsenic. The technology typically can reduce arsenic concentrations to less 10 ppm. Its effectiveness is sensitive to a variety of untreated water contaminants and characteristics. The adsorption media is usually packed into a column. As the contaminated water is passed through the column, contaminants are adsorbed. When adsorption sites become filled, the column must be regenerated or disposed of and replaced with new media. Aluminum oxides, iron oxide/hydroxides, titanium dioxide, cerium oxide, granular iron hydroxide/oxide, commercial titanium dioxide, cerium oxide and manganese dioxide can be used as effective adsorbents for arsenic removal [5,104,109,125,144-148].

Activated alumina was the first adsorptive medium to be successfully applied for the removal of arsenic from water supplies [149,150]. Several different studies have established with greater than 98% of arsenic removal with activated alumina [151-153]. Some of the activated alumina based sorptive media include BUET Activated Alumina, Alcan Enhanced Activated Alumina, Arsenic Removal Units (ARUs) of Project Earth Industries Inc., USA, and Apyron Arsenic Treatment Units [154,155]. Recently, Ike *et al* have examined the efficacy of activated alumina in removing arsenic through bacterial oxidation of As(III) with a chemical adsorption process [156].

Adsorption on iron based sorbents is an emerging treatment technique for arsenic removal. The currently available sorbents in the market includes granular ferric hydroxide, zero valent iron, iron coated sand, modified iron and iron oxide based adsorbents. The sorption process has been described as chemisorption which is typically considered to be irreversible and leads with better performance than activated alumina [157-162]. Hussm *et al* have developed a simple and effective arsenic filter based on composite iron matrix (zero valent iron) and won the prestigious Grainger gold medal award for their work [163]. Recently, Katsoyiannis *et al*) studied the kinetics and mechanism of Fenton reagent generation and As(III) oxidation and removal by ZVI in the pH range 3-11 in aerated water [164].

There are several filters available that use indigenous material as arsenic adsorbent. Red soil rich in oxidized iron, clay minerals, iron ore, iron scrap or fillings and processed cellulose materials are known to have capacity for arsenic adsorption. Some of the filters manufactured using these materials. Milton *et al* have examined the effectiveness of three pitcher filters used in Bangladesh [165].The Garnet home-made filter contains relatively inert materials like brick chips and sand as filtering media. No chemical is added to the system. The Chari filter also uses brick chips and inert aggregates in different Charis as filter media. The effectiveness of this filter in arsenic removal is not known.

The Shafi and Adarshs filters use clay material as filter media in the form of candle. The Shafi filter was reported to have good arsenic removal capacity but suffered from clogging of filter media. The Adarsha filter participated in the rapid assessment program but failed to meet the technical criterion of reducing arsenic to acceptable level [154]. Bijoypur clay and treated cellulose were also found to adsorb arsenic from water [166]. Two household filters tested at BUET laboratories include Chiyoda Arsenic Removal Unit, Japan, and Coolmart Water Purifier, Korea [155]. Ko *et al* have used colloidal iron oxide coated sand based treatment unit for arsenic removal [167]. Cornejo *et al* has presented an in situ arsenic removal method applicable to highly contaminated water based on zerovalent iron (steel wool), lemon juice and solar radiation [168].

The technology is very simple, does not require chemical addition and is useful at community or household levels. However, despite their simplicity, the adsorption methods usually fail in lowering arsenic concentration to acceptable levels, and are recommended to treat with water at low Fe/As content. Several constituents can interfere with the adsorption process, either by competing for adsorption sites or clogging the media with particulate matter [109].

#### 1.10.1.6. Membrane Processes

Membrane technology can remove a wide range of contaminants from water. This technology typically can reduce arsenic concentrations to less than 50 ppb and in some cases to below 10 ppb. However, its effectiveness is sensitive to a variety of untreated water contaminants and characteristics. It also produces a larger volume of residuals and tends to be more expensive than other arsenic treatment technologies. There are four types of membrane processes: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). All the four processes are pressure-driven and are categorized by the size of the particles that can pass through the membranes or by the molecular weight cut off (i.e., pore size) of the membrane [149,150]. Because arsenic species dissolved in water tend to have relatively low molecular weights, only NF and RO membrane processes are likely to effectively treat dissolved arsenic [150].

Reverse osmosis is the oldest and best technology for removal of arsenic in small-scale processes [101]. The membranes in reverse osmosis contain extremely small pores (<0.001 μm) [169]. Oxidation of arsenite is not recommended in reverse osmosis because the use of an oxidising agent may damage the membrane. The advantage of reverse osmosis is that it does not use chemicals, and it is an effective means of removing As(V). The production of only small amounts of treated water, its high cost and large energy consumption are some of its disadvantages. The use of reverse osmosis in developing countries is hampered due to the expense and the high consumption of energy by the technology. Oh *et al* applied reverse osmosis and nanofiltration membrane processes for the treatment of arsenic contaminated water applying low pressure by bicycle pump [170].

Nanofiltration is also a high-pressure process and has the ability to remove dissolved As(V) due to the small pore size of the membrane [101]. The mechanism of nanofiltration is removal of uncharged components by size exclusion and separation of ionic species due to the nature of the membrane. The effect of pH on arsenic species removal by nanofiltration was studied [171]. The removal efficiency of arsenate increased significantly with increasing pH. Xia *et al* have also investigated removal efficiency of arsenic from synthetic waters by nanofiltration (NF) membranes in China [172]. Nanofiltration processes need less pressure for operation than does reverse osmosis. This has an advantage of saving energy.

Microfiltration is a low-pressure separation technique. The pore size in microfiltration is so large that it cannot easily remove dissolved arsenic or colloidal arsenic species; however, particulate forms of arsenic can be removed by microfiltration [101]. As a result, microfiltration is highly dependent on the size distribution of arsenic-bearing particles. Since the presence of particulate arsenic in water is very limited, coagulants and flocculants are often added to increase the arsenic particle size [173].

### 1.10.1.7. Ion exchange Resins

Ion exchange is a physical-chemical process in which ions are swapped between a solution phase and solid resin phase. The solid resin is typically an elastic three-dimensional hydrocarbon network containing a large number of ionizable groups electrostatically bound to the resin. These groups are exchanged for ions of similar charge in solution that have a stronger exchange affinity (i.e. selectivity) for the resin. Ion exchange has been suggested as the best technology for arsenic removal from drinking water [174]. Different categories of synthetic resins can be used for arsenic removal. The process is similar to that of adsorption; just the medium is a synthetic resin of more well defined ion exchange capacity. Few manufacturers have developed synthetic resins suitable for arsenic removal. However, the resins need to be replenished after use and renewal interval is dependent on the quantity of arsenic in water [175].

Chanda *et al* impregnated iron to weak base macroporus chelating resin to remove As (III) and As (V), the results showed that As (III) and As (V) were prior to other anions reacting with the resin at a low level of As [176]. Lenoble *et al* loaded manganese dioxide on a polystyrene matrix anionic commercial resin in chloride form, called R-$MnO_2$, which was tested for As(V) retention and for As(III) simultaneous oxidation and removal [177]. Luis reported the nanoparticle loaded iron hydroxide on the polymer resin producing four polymers (HCIX-M, HCIX-G, HAIX-M,HAIX-G) to remove arsenic [178]. Liu *et al* prepared a new type of ion exchange fiber to remove arsenate from water [179]. Greenleaf *et al* loaded nanoparticle hydrated iron oxide

(HFO) on ion exchange fiber to sorbed arsenic [180]. Tetrahedron ion exchange resin filter tested under rapid assessment program in Bangladesh showed promising results in arsenic removal [154].

Current commercial ion exchanger was prone to be saturated because of its poor selectivity to arsenic and suffered from competing with other anions. Due to the lack of As-selectivity, current ion exchange required frequent regeneration and lots of regeneration brine was used, which in turn resulted in a large quantity of volumes wastewater containing arsenic [174]. Therefore, the ion-exchange fibers have many advantages such as higher specific surface area, smaller diameter, and better elasticity; they may occur in the form of filaments and other textile articles and can be regenerated and reused [178]. Disadvantages of ion exchange as a treatment technology include: generation of toxic chemical reagents and their release into the environment. Efficiency can be reduced if there are competing ions present, and arsenic can be released to the treated water if the system fails [101].

#### 1.10.1.8. Electrochemical Methods

The electro-coagulation process was first applied for drinking water on a large scale in the US in 1946 [181]. It is a simple, efficient and promising technique that does not require the addition of any chemical. In this process, flocculating agent is generated by electro oxidation on anode, which is made up of metal, generally iron or aluminum. Several researchers reported maximum arsenic removal (more than 99.6%) by aluminum and iron electrodes [182-185]. A system with the combined use of both aluminum and iron in the same electrochemical cell has been published [186].

The removal efficiency of both arsenic species with the electrocoagulation was more than 90% at different conditions [187]. The major advantage of this method is that it has applicability for the removal of both species of arsenic, i.e., arsenite and arsenate. Removal efficiency is highly dependent on the current density, pH, conductivity, particle size, type of electrode, aqueous medium chemistry and presence of air injection [183]. There is no evidence reported in the literature regarding regeneration of electrode for this purpose.

Electrodialysis (ED) is a process in which ions are transferred through alternating ion exchange membranes under the influence of direct electric current. The ions travel from a lesser to a higher concentrated solution. Very few procedures have been conducted to evaluate this process for the removal of As [188]. The major disadvantage of this process is routine maintenance, which consists of changing cartridge filters, calibrating and maintaining instruments, replacing membranes, maintaining pumps and valves as well as replacing electrodes. The systems, however, are typically more expensive than NF and RO systems [189]. Garrido *et al* developed capacitive deionization (CI), an advanced electrochemical method based on the deionization by flow through a capacitor like system with electrostatic load, configured as a low-cost filter of coal electrodes. This technology is recommended for arsenic removal with less than 3000 ppm of TDS [190].

### 1.10.2. Emergent Technologies

In the last decades, a large amount of scientific and technological work has been devoted to develop new technologies for arsenic remediation that seek to minimize costs of investment, operation and maintenance (i.e., low-cost technologies) and technological development (i.e., low-tech systems). These technologies focus more on small scale or household treatments for isolated populations. However, the social acceptance, waste production and treatment and the corresponding required handling needs to be assessed before considering the implementation of each remediation option. Some of these technologies are merely adaptation of conventional methods like coagulation–filtration, or adsorption, using very cheap materials (iron-coated sand, bricks, iron filings, activated alumina or carbon) to be employed at household or community scale [191,5]

### 1.10.2.1. Biological Method

Biological treatment is currently receiving attention for the removal of arsenic species from contaminated waters. The advantage of biological treatment physico-chemical treatment methods is that it uses microorganisms instead chemicals to reduce/oxidise or remove contaminants. Microbial activity can remove, mobilize and contain arsenic through coprecipitation, sorption, complexation, oxidation-reduction and biomethylation, demethylation processes. A variety of microorganisms may be involved in biological treatment.

Fungi and biomass from *Rhizopus oryzae,* dead fungal biomass *P. chrysogenum* (Mycan), *Lessonia nigrescens* (an algae), *Aspergillus niger* (fungus) coated with iron oxide, *Penicillium purpurogenum* were used for arsenic removal and the pre-treatment with hexadecyl-trimethyl ammonium bromide (HDTMA-Br) dodecylamine and a cationic polyelectrolyte was carried out to improve arsenate biosorption [192-198]. One such group of microorganisms is the sulphate-reducing bacteria (SRB) that have been used for the treatment of contaminated mine waters [199]. Rittle *et al* studied the precipitation of arsenic during bacterial sulphate reduction to sulphide [200]. Kirk *et al.* (2004) showed the presence of sulphate-reducing bacteria in groundwater could reduce the level of arsenic [201].

Phytoremediation has been proposed as a cost effective methods for removal of arsenic from soil and water [202,203]. Young plants of water lettuce, *Garcinia* *combogia* (indigenous plant), *Pista stratiotes* L. (aquatic plant), water hyacinths (*Eichhornia crassipes*) and dried roots of water hyacinths (harvested from a pollution free pond and hydroponically cultured) were used for the simultaneous and rapid remediation of arsenic, cadmium, mercury and lead from polluted water at effective concentration [204-206]. *Pteris vittata* and *P. cretica* of the same age were recently used for arsenic phytofiltration applicable at below new drinking water limit of 10 ppb [207,208]. Human hair has also been applied to remove arsenic due to their ability to absorb arsenic from contaminated water [209].

#### 1.10.2.2. Polymeric Materials

Polymers with chemically active functional groups create a unique combination of properties. Polypyrrole, polyaniline and polythiophene are three of the most well known conducting electroactive polymers used for the arsenic removal attracting a great deal of attention in the last two decades. For the selective binding of arsenic from the water, polymeric materials have been investigated and patented successfully [210]. The chelating polymers designed either by the polymerization of monomers possessing the desired sites (i.e. nitrogen, oxygen or sulphur) or by reaction with low molecular weight compounds containing different functional groups (i.e. $–NH_2$, $–SO_3H$, $–NH_4OH$, –SH and many others). The available free coordination sites of chelating polymers usually binds with metal ions through coordinate or coordinate-covalent bonds.

Poly(3-acrylamidopropyl) trimethylammonium chloride hydrogels were utilized as absorbents for the removal of toxic arsenate from aqueous medium [211]. The mercaptyl resin, poly(ethylene mercaptoacetimide) (PEM), can remove arsenate and arsenite anions by redox sorption in acidic and alkaline media, respectively. The PEM resin prepared by the Schotten-Baumann reaction of polyethyleneimine with mercaptoacetyl chloride was determined to have a redox capacity of 8.26 meq/g dry resin [212]. Rivas *et al* investigated the new class of water soluble tin containing PAA matrix. Presumably, the Sn(II) ions coordinate through 2-4 carboxylate groups by a conventionally bidentate structure is applied to retain and separate arsenite from water [213]. A new hybrid adsorbent of titania–silica binary oxide-polyacrylonitrile (PAN) has been fabricated by loading nanosized sol–gel-derived $TiO_2$–$SiO_2$ onto a porous PAN polymer for enhanced As(III) and As(V) species removal from aqueous media. The prepared hybrid adsorbent exhibited highly selective arsenic retention from water in the presence of other ions at much greater levels than those toxic metals examined [214].

It is well established that As(III) has a strong affinity toward mercaptan (thiol) groups existing in biomolecules such as amino acids, peptides and proteins (including some enzymes), which explains the higher toxicity of this species for human being [215-217]. Based on the above understanding, some thiol-based polymers including resins, adsorbents have been investigated by several authors [218-222]. These studies suggest that materials bearing thiol functional groups are very promising, and suitable alternate for specified As(III) removal. PVA based mercaptyl fibers, coated on a fiber glass substrate, for the purpose of removing As(III) from water The fibrous mercaptyl system's performance is compared to the commercial product, Duolite's GT-73, a macroreticular polystyrene–divinylbenzene resin with chelating thiol functional groups [223]. Thiol-functionalized mesoporous PVA/$SiO_2$ composite nanofiber membranes were applied for the adsorption of heavy metal ions from aqueous solution [224]. Huge class of natural polymers and their derivative have been frequently used for arsenite separation. Chitosan, chitin, chitosan/chitin mixture and their other modified derivative used for arsenic removal from contaminated drinking water [224,226].

Further studied the sorption of As(V) on molybdate-impregnated chitosan gel beads with an increased sorption capacity over raw chitosan for As(V) [227]. Chitosan beads are also reported to remove As(III) and As(V) in both batch and continuous process from water. Recently, removal of both As(III) and As(V) by chitosan-coated alumina or molybdate-impregnated chitosan was reported [228]. Chitosan was also used as a resin for arsenic sorption in column studies with improved resistance to shrinkage which was obtained by crosslinked chitosan functionalized with 3,4-diamino benzoic acid [229]. Boddu et al. used ceramic alumina dip-coated with chitosan for As(III) and As(V) removal in column and an improved sorption capacity was reported for As(III) [230]. Daniel *et al* reported a newly developed iron-impregnated chitosan granular adsorbent for arsenic removal [231].

Native cellulose, arisen as crystalline microfibrils, constitutes the most abundant and renewable polymer resource available worldwide. These modified cellulose fibers were presented as effective adsorbents for removing $F^-$, $AsO_2^-$ and $AsO_4^{3-}$ from aqueous solutions While the competing anions exist, the $F^-$ removal proportions decreased from 81.81% to 27.56%, and the As removal proportions remain still above 99%. The application of biopolymers (alginate), as sorbent supports, for the removal of arsenic from contaminated water has been investigated in the present study [232]. The natural fibrous polymeric materials, viz., jute, coconut coir and alasca are used for the arsenic remediation too [233].

## 1.11. Regeneration Process

The polymeric material appears to be economically more feasible, due to the reused property of polymer. Three major methods for regeneration of the polymeric agent are known: Chemical, thermal and electrochemical regeneration methods. In chemical method, regeneration is possible by the change in pH, trans complexation with another one and the metal ions can be reduced, thus facilitating the subsequent separation step. In electrothermal regeneration, electrolysis of the retentate results in a deposition of the metal on an electrode, whereas the polymer reagent remains as it is in the system. However, electrochemical regeneration appears to be more energy-consuming than the chemical one. In thermal regeneration, the polymer metal bond can be cleaved by heating the retentate. This method seems to be restricted to few cases [234]. Sudipta *et al* investigated the regeneration ability of ArsenX$^{np}$ is amenable to reuse for multiple cycles without any significant loss in removal capacity [235].

As we know that arsenic is a natural metalloid and found in the atmosphere, soils and rocks, natural waters and organism permanently. It cannot be completely removed from the environment only can be transformed from one form to another from. One should also realize that arsenic mitigation strategy should be location specific. A method suitable for a specific area should not be generalized for the other affected regions due to geographical variations and different socio-economic conditions of people. Arsenic removal technologies have to compete with other technologies in which cost appears to be a major determinant in the selection of a treatment option by the users. All the technologies discussed in this chapter have their own merits and demerits and should be refined to make them suitable and sustainable for a particular situation.

The modifications should be based on the pilot-scale implementation of the technologies with the objectives to:

- Improve effectiveness in arsenic removal
- Reduce the capital and operation cost of the system
- Make the technology user friendly
- Overcome maintenance problems
- Resolve sludge and arsenic concentrates management problems.

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The overall goal of this research is to develop a new PVA based chelating material for specific removal of arsenite from water under various conditions. The specific objectives are to:

1. Modify PVA by esterification with thioglycolic acid and introduce the SH group in the matrix which is responsible for the arsenite chelation.
2. In addition, the thiolated PVA get crosslinked with different crosslinkers to improve the water resistance of material with the help of crosslinking of OH groups of PVA.
3. After optimizing all the varying conditions, the resulting crosslinked thiolated PVA will be used for selective binding of arsenite. Various removal affecting parameters will be observed.
4. Derived chelating material has very good regeneration ability which makes cost effective material for this purpose. The regeneration ability has been studies under different conditions.
5. To investigate additional feature of the TPVA in water treatment.

The work described in this Ph.D. thesis is divided into six main sections.

Chapter I of the thesis deals with the background history of arsenic, respective properties, uses, mobilization, toxic effects on humans and detection methods. A complete review of various methods used for arsenic removal has been presented. The merits and demerits of all the technologies have also been discussed.

Chapter II of the thesis deals with the modification of polyvinyl alcohol (PVA) by esterification process. PVA get esterified with thioglycolic acid (TGA) at different reaction parameters. The influence of reaction parameters such as PVA concentration, TGA concentration, reaction time, reaction temperature and catalyst concentration on the thiol content was investigated. A correlation between reaction parameters and the thiol content has been established.

Chapter III of the thesis deals with the crosslinking studies of thiolated polyvinyl alcohol. The derived thiolated PVA have been crosslinked with different nature of crosslinker. The influence of various crosslinking parameters such as TGA concentration, crosslinker content, and crosslinking time was investigated. Swelling study of the samples was observed in different pH media and swelling time. A correlation between crosslinking, thiol content and swelling has been established.

Chapter IV deals with the characterization of pure PVA and crosslinked thiolated PVA using various techniques, such as DSC, TGA, XRD and TG-FTIR. The influence of the TGA concentration and different crosslinker on the structural changes of PVA has been monitored.

Chapter V of the thesis deals with the application of novel PVA based chelating material bearing thiol groups for arsenite removal from water. Batch experiments were applied to evaluate the As(III) removal performance of the chelating material.

The influence of several parameters such as pH, compositions of components, contact time, presence of competitive ions and different water samples were investigated for the As(III) removal from water. The regeneration ability and antifungal activity was also observed.

Chapter VI summarizes the work highlighting the important findings of the present investigation.

# Chapter-2

# POLYVINYL ALCOHOL (PVA) MODIFICATION BY ESTERIFICATION WITH THIOGLYCOLIC ACID (TGA)

## 2.1. Introduction

Polyvinyl alcohol (PVA) is the most interesting commercially used polymer that has been studied intensively in diverse areas of science technology development i.e. biomedical applications, fuel cell membranes, water treatment, and commodity materials as an adhesive for paper, textiles and leather industries [1-12]. PVA is synthesized by the polymerization of vinyl acetate monomers into poly(vinyl acetate) followed by the hydrolysis of the acetyl groups into PVA. It is soluble in water where the optimum conditions for dissolutions are primarily governed by the degree of hydrolysis, molecular weight, particle size distribution and crystallinity. PVA modification can be carried out by various routes which could be beneficial tool for obtaining PVA with new properties and therefore increasing the scope of their applications. Esterification is a very useful alternative for PVA modification by using various acid and their derivatives**.** The esterification is a chemical reaction that involves two reactants, an alcohol and an acid in the presence of a catalyst, to give an ester and water as the product.

The chemistry of PVA is largely concerned with ester formation by reaction with acid chlorides or acid anhydrides. Schotten-Baumann esterification of PVA has been reported with cinnarnoyl chloride for the preparation of poly(vinyl cinnamate) for industrial use [13]. Gung, *et al.* stated that the esterification of PVA with acryloyl chloride formed PVA-AA which contains ethylene group in addition to the ester bond [14]. The PVA esterification is carried out with polyacrylic acid and the esterified membrane is used as ion exchange semi IPN-membrane [15]. Castenheiro *et al* used PVA as catalytic membrane containing sulfonic acid group for the esterification of acetic acid by isoamylic alcohol [16]. The simplest pH-sensitive hydrogels can be prepared by repetitive freezing and thawing cycle process of the PVA and PAA [17].

Giménez *et al* studied the PVA esterification with 10-undecenoyl chloride in presence of pyridine as a catalyst use for the polymer modification [18]. PVA esterification with boric acid has been reported for lipase entrapment in PVA matrix [19]. The production of vinyl alcohol-vinyl ester copolymers was reported by the esterification of PVA with phthalic and succinic anhydrides in presence of 1,4-butanediolglycidylether as crosslinker [20]. Therefore, the modified crosslinked PVA shows good swelling property and is considered as superabsorbent hydrogels. Recently PVA esterification with trimellitate in presence of 4-(*N,N*-dimethylamino) pyridine and triethylamine as a catalyst was studied for the preparation of reversible thermo-swelling gel [21]. Shi *et al* reported the esterification reaction between PVA/starch and citric acid during molding at 140 °C at different reaction conditions. Citric acid acted not only as a plasticizer, but also helps in PVA crosslinking by ester formation. The resulting product was successfully used for cell growth [22]. Quintero *et al* studied the esterification of PVA with PAA under the mild conditions leads the formation of a 3-D network whose degree of crosslinking depends on the conditions of the thermal treatment, such as, temperature, duration and pressure [23]. The fabrication of Starch–maleate–polyvinyl alcohol (SMP) hydrogels have been prepared by reacting PVA with maleic acid (MA) substituted sago starch (SS). Resulting PVA ester hydrogel was envisaged in biomedical application [24].

Thioglycolic acid (TGA) is a thiol derivative of glycolic acid and it has the characteristic smell associated with the vast majority of sulfur compound while its toxicity is not significantly higher than that of propanoic acid [25]**.** Thiols are stronger acids than relevant alcohols and phenols, their sulfur group will easily react in the presence of acid, ketones or organic halogens. It is a useful chemical intermediate in the chemical reactions such as addition, elimination and cyclization. The applications of thioglycolic acid and its derivatives are wide in the fields of PVC stabilizers, down-hole acidizing, corrosion inhibition in the oil field industry, manufacturing of pharmaceuticals, agrochemicals and dyes, shrink-resistant treatment of wool, fabric dyeing, leather processing, cosmetics and depilatories [26-28]. Very few citations have been available for the involvement of thioglycolic acid in esterification. Their respective esters are key materials in various fields because they are able to react and remain stable for a longer length of time. Dicharry *et al*, reported the multifunctional macromolecular thiol (TPVA) obtained by esterification of (PVA) with 3-mercaptopropionic acid and was used as a wheat gluten (WG) reactive modifier [25]. Moreno *et al* reported the esterification reaction in between the hydroxyl group of PVA and carboxylic group functionalized gold nanoparticles which were synthesized by the reaction of mercaptoundecanoic acid and hydrogen tetrachloroaurate [29].

Catalyst is used in the esterification process to enhance or accelerates the chemical reaction process. The catalysts essentially promote the protonation of the carbonyl oxygen on the carboxylic group, thereby activating nucleophilic attack by an alcohol to form a tetrahedral intermediate. Disproportionation of this intermediate complex ultimately yields the ester. In spite of the long history of esterification and the large amount of literature concerning the performance and kinetics of various catalysts, there are still many fundamental issues that remain poorly understood. For instance, an important subject that needs to understand the effect of produced water from esterification in acid catalysed reaction. In further continuation, it can be divided into two categories, homogenous and heterogeneous catalyst. Homogenous catalysts such as the strong liquid mineral acids, such as sulphuric acids [30], orthophosphoric acid, toluenesulfonic acid, tin chloride (lewis acid) and hydrochloric acid [31]. Heterogeneous catalyst such as phosphotungstic acid [32].

In the present work, we attempted to modify PVA by esterification using TGA. Esterification was carried over sulfuric acid as a catalyst. The effect of reaction time, reaction temperature, PVA concentration, TGA concentration and catalyst concentration was studied. The optimization of reaction conditions for the process of esterification was carried out.

### 2.2. Experimental

#### 2.2.1. Materials

PVA (Mw. 1,50,000 and the degree of hydrolysis 85%) was supplied from Sigma. Thioglycolic acid (TGA), sulfuric acid ($H_2SO_4$) and methanol (HPLC grade) were purchased from Merck, India. All were used without further preparation. While TGA has the characteristic smell associated due to the presence of sulfur, its toxicity (according to the MSDS) is not significantly higher than that of propionic acid. Ultra-pure water, resistivity less than 18 MΩcm, produced by a Millipore Milli-Q system was used throughout the experimental work.

#### 2.2.2. Esterification Reaction

Homogenous solution of 2 wt% PVA was prepared by dissolving 2 g PVA powder in 100 ml water under vigorous stirring for overnight at room temperature. Mixture of TGA and $H_2SO_4$ of different compositions was added slowly in PVA solution with varying reaction parameters. After completion of the reaction, the mixture was slowly poured into methanol. The white precipitate was the collected, washed repeatedly by methanol and dried under vacuum oven at room temperature.

#### 2.2.3. Thiol Content Estimation

The amount of the involved and accessible thiol groups was determined according to a protocol based on the previously reported *Volhard's silver nitrate method* [10]. The determination is based on the chemical affinity of silver by thiol groups. This method do not cause any water biased during thiol estimation [33]. Following the protocol, 50 mg of dried thiolated polyvinyl alcohol (TPVA) and immersed in 50 ml of 0.01 M silver nitrate solution. The flasks were covered to avoid exposure to light and stirred in a shaker for 3 h prior to testing. The remaining silver nitrate was titrated with standardized 0.01 M potassium thiocyanate (KSCN) using iron ammonium sulfate hexahydrate as an indicator. The endpoint was detected when an excess of thiocyanate anion formed a red colored complex with the iron compound. The thiol content was expressed in mmol/g of polymer. In all cases, the tests were carried out in triplicate measurement.

**Steps:**

$$\underset{\textbf{(Modified Polymer)}}{\sim RSH} + AgNO_{3(aq)} \longrightarrow \sim RSAg_{(S)} + HNO_{3(aq)} \qquad \textit{eq. 1}$$

**Titration step**

$$AgNO_{3(aq)} + KSCN_{(aq)} \longrightarrow AgSCN_{(S)} + KNO_{3(aq)} \qquad \textit{eq. 2}$$

**End point**

$$6SCN^{-}_{(aq)} + Fe^{3+}_{(aq)} \longrightarrow \underset{\textbf{(Red complex)}}{Fe(SCN)_6{}^{3-}_{(aq)}} \qquad \textit{eq. 3}$$

### 2.2.4. Swelling Studies

The swelling studies of the TPVA were carried out by measuring the amount of water incorporated into the sample. Pre-dried sample was immersed in MilliQ water having pH 7 at swelling temperature 40 °C. The sample was taken out from water at certain time intervals and weighed after blotting out the excess of water from the surface of sample with tissue paper. They were put back in water immediately after weighing. The swelling behavior of the sample was monitored as a function of time. The water absorption of the sample was calculated as the percent swelling by following equation [34]:

$$\text{Swelling (\%)} = \frac{W_s - W_d}{W_d} \times 100 \qquad \textit{eq. 4}$$

Where, $W_s$ and $W_d$ are the weight of the samples in the swollen and dry states, respectively.

### 2.2.5. Attenuated Total Reflectance- Infrared Spectroscopy (ATR-IR)

The ATR-IR spectra of samples were recorded on Bruker Alpha P(Opus 65) spectrophotometer. The spectra of films were recorded over the 400-4500 $cm^{-1}$ range.

## 2.3. Result and Discussion

The esterification process of PVA has been carried out with the TGA in the presence of $H_2SO_4$ as a catalyst at different reaction conditions. The schematic representation of the esterification process is presented in Figure 2.1. Reaction starts below and gets completed at 60ºC as monitored by decrease in thiol content. The reactivity of PVA is strongly affected by the bulky hindrance of the –OH group which is responsible for the interaction with others reactive groups.

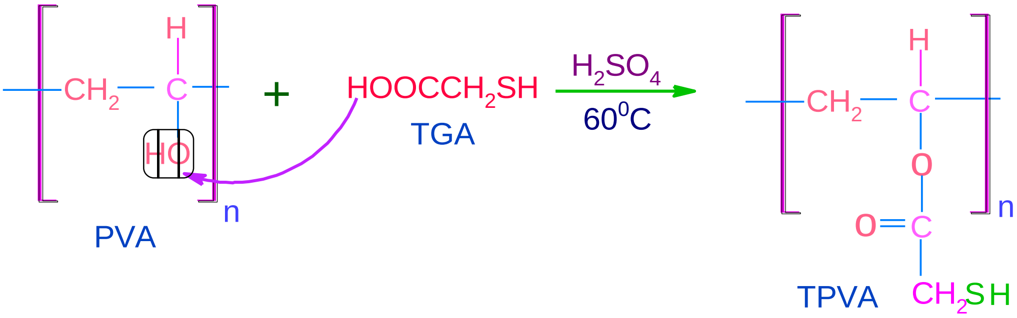

**Figure 2.1. The optimized schematic representation of the esterification reaction.**

As a result, the hydroxyl groups of PVA react with the carboxyl groups of TGA and form TPVA are having –SH group in the matrix. The reaction has been carried out under homogeneous conditions with $H_2SO_4$ as a catalyst and the effects of varying reaction conditions viz, reaction time, reaction temperature, PVA concentration, TGA concentration and catalyst concentration on thiol content have been investigated.

### 2.3.1. Influence of the PVA Concentration

The effect of PVA concentration on the thiol content in esterification reaction in feed mixture is investigated in Figure 2.2 and Table 2.1.

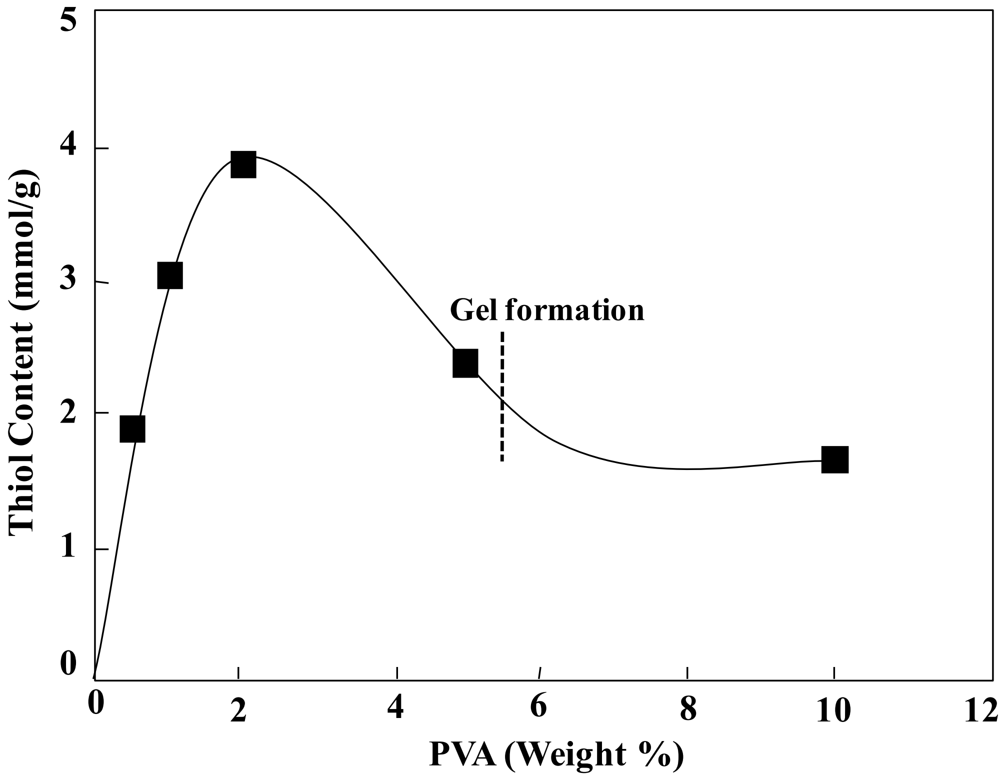

**Figure 2.2. Variation of the thiol content with the PVA concentration. Reaction conditions: TGA concentration, 25%; $H_2SO_4$ concentration, 1%; reaction temperature, 60 °C; reaction time, 24 h.**

**Table 2.1. Variation of the thiol content with the PVA concentration. Reaction conditions: TGA concentration, 25%; $H_2SO_4$ concentration, 1%; reaction temperature, 60 °C; reaction time, 24 h.**

| PVA Concentration (%) | Thiol Content (mmol/g) |
|---|---|
| 0.5 | 1.9 |
| 1 | 2.8 |
| 2 | 3.9 |
| 5 | 2.4 (slightly gel) |
| 10 | 1.7 (gel) |

As the alcohol concentration increases, thiol content showed an increasing pattern from 0.5 to 2% (w/v) concentration and beyond this point, thiol content shows decreasing trend. At 10% PVA concentration the complete gel formation take place and the viscosity measurement was not possible. The reaction could not be monitored beyond 10% PVA concentration due to the gel formation which leads to severe restriction to TGA diffusion within the viscous gel medium [35]. This leads to limited interaction in between acid and base. As a result, the thiol content decreases significantly. From the above statement, 2% (w/v) PVA concentration was optimized for further reactions.

### 2.3.2. Influence of the Reaction Time

The variation of the reaction time in the esterification of PVA is a more effective parameter. The effect of reaction time on the thiol content in esterification reaction is presented in Figure 2.3 and Table 2.2.

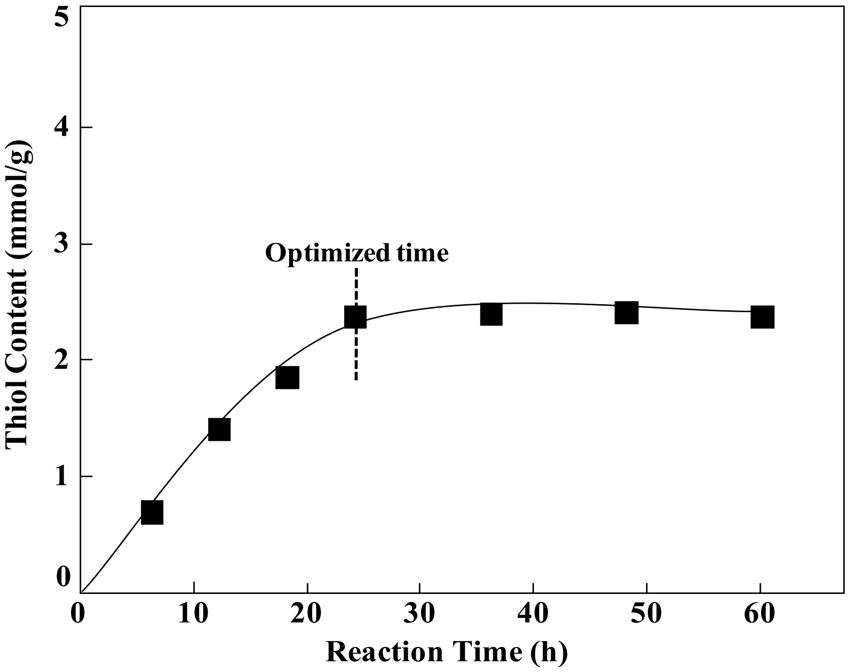

**Figure 2.3. Variation of the thiol content with the reaction time. Reaction conditions: PVA concentration, 2%; TGA concentration, 5%; $H_2SO_4$ concentration, 1%; reaction temperature, 60 °C.**

**Table 2.2. Variation of the thiol content with the reaction time. Reaction conditions: PVA concentration, 2%; TGA concentration, 5%; $H_2SO_4$ concentration, 1%; reaction temperature, 60 °C.**

| Reaction Time (h) | Thiol Content (mmol/g) |
|---|---|
| 6 | 0.72 |
| 12 | 1.43 |
| 18 | 1.88 |
| 24 | 2.40 |
| 36 | 2.43 |
| 48 | 2.44 |
| 60 | 2.40 (slightly gel) |

The time required to achieve equilibrium esterification depends on the nature of the alcohol used. It has been observed from previous study that, if the chain length of the alcohol is larger than rate of reaction become slow, due to the fact that the lesser number of hydroxyl groups interact with carboxyl groups of the respective acid [32]. Hence, the TGA does not penetrate into the bulk of the larger PVA molecule, it takes longer time for reaction. Initially, TGA is having the characteristic smell (due to the presence of sulfur) and thereafter the smell gets distant which indicates the completion of the reaction.

The plot shows a sharp increase initially and tends to level off beyond 24 h. The thiol content reaches equilibrium within 24 h. A maximum thiol content of 2.65 mmol/g was achieved under our experimental conditions. The reaction began to slow down afterwards, which might be due to the aggregation of the produced water favouring the reverse reaction (hydrolysis). Shanmugam *et al* reported that the longer time did not support the change in the final product of the reaction and a noteworthy change was observed at 24 h reaction time [32]. After 24 h, reaction reaches their equilibrium, therefore reaction time variation was optimized for further process.

### 2.3.3. Influence of the TGA Concentration

In esterification process, the consumption of alcohol was strongly dependent on the acid concentration therefore, higher concentration of acid favored the ester formation. The effect of varying the ratio of TGA on the thiol content in esterification reaction is investigated in Figure 2.4 and Table 2.3. In our study, the acid concentration variation was observed from 5 to 25% with respect to PVA concentration. The continuous increment of acid in the feed reaction mixture leads to higher thiol content. The reaction was not monitored beyond 25% TGA concentration due to the high exothermic nature of the reaction and lower boiling point of the TGA. 25% TGA was taken as the optimized concentration of TGA at maximum thiol content 3.9 mmol/g.

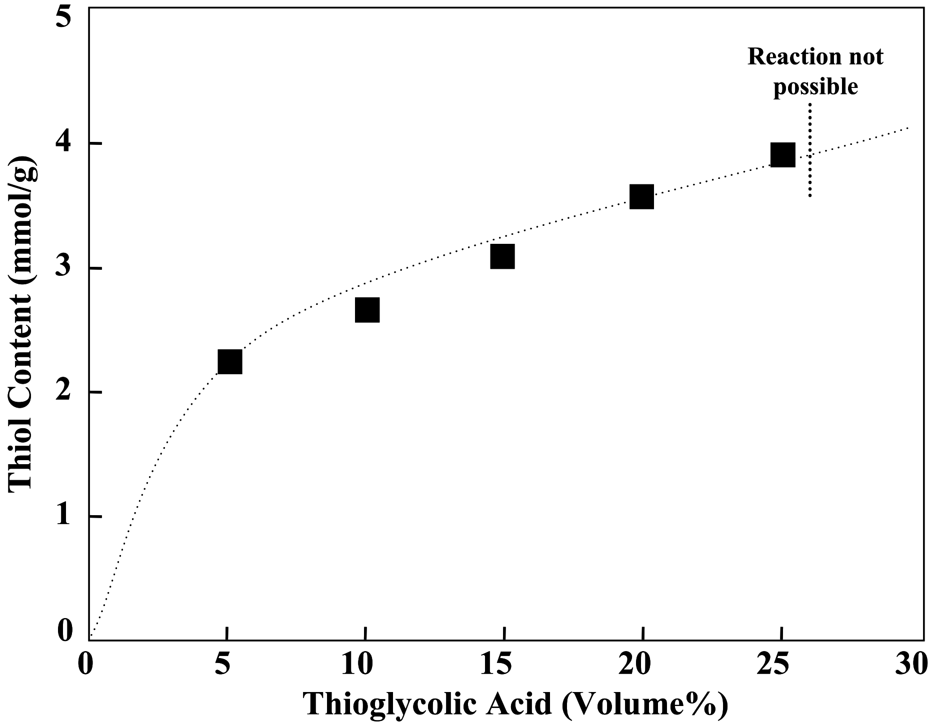

**Figure 2.4. Variation of the thiol content with the TGA concentration. Reaction conditions: PVA concentration, 2%; $H_2SO_4$ concentration, 1%; reaction temperature, 60 °C; reaction time, 24 h.**

**Table 2.3. Variation of the thiol content with the TGA concentration. Reaction conditions: PVA concentration, 2%; $H_2SO_4$ concentration, 1%; reaction temperature, 60 °C; reaction time, 24 h.**

| TGA Concentration (%) | Thiol Content (mmol/g) |
|---|---|
| 5 | 2.4 |
| 10 | 2.6 |
| 15 | 3.1 |
| 20 | 3.6 |
| 25 | 3.9 |

### 2.3.4. Influence of the Reaction Temperature

The influence of the reaction temperature on the thiol content is presented in Figure 2.5 and Table 2.4. The reaction was carried out in the temperature range of 50-80 °C to investigate the esterification process. The thiol content trend is strongly influenced by the reaction temperature. Thiol content increases very slowly, accelerates subsequently with increasing acid concentration and then tends to reach saturation at 25% TGA.

Interestingly, the thiol content was very close to each other when reaction was carried out in the range of 60–80 °C. It seems that the thiol content decreases due to the possibility of *in-situ* cross-linking. It may be mentioned here that the PVA consists of the reactive –OH groups and each one of these –OH group participates in the modification. At lower temperature, the generated heat is not sufficient for the interaction of reacting groups. While at moderate temperature the present hydroxyl groups become active and easily take part in the esterification reaction by involving pendent –OH groups.

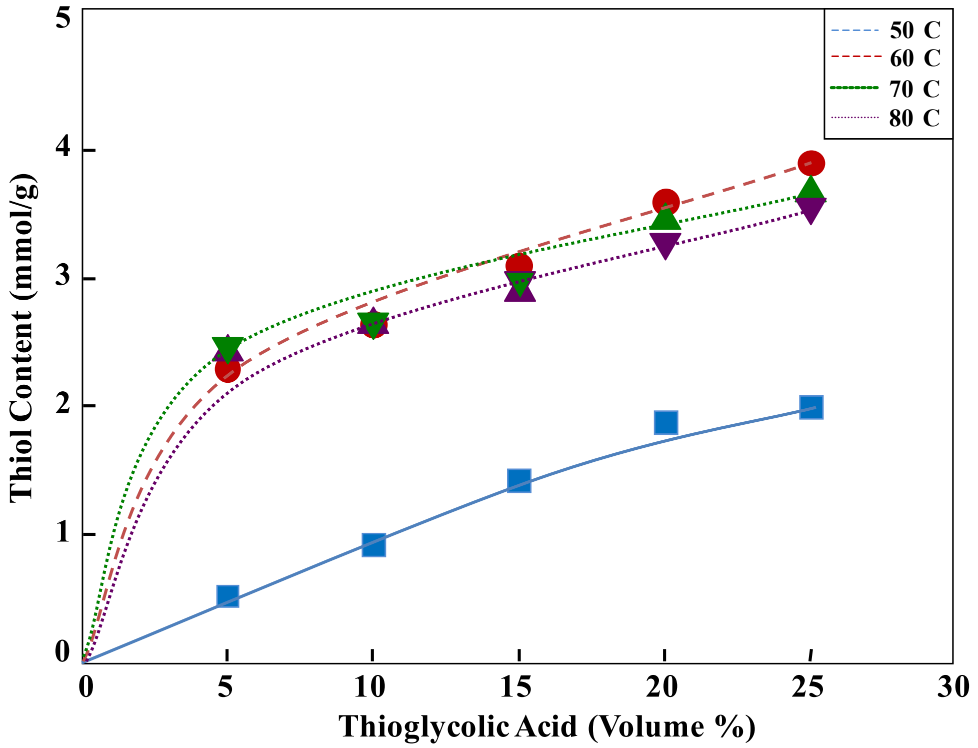

**Figure 2.5.** **Variation of the thiol content with the TGA concentration and reaction temperature. Reaction conditions: PVA concentration, 2%; $H_2SO_4$ concentration, 1%; reaction time, 24 h.**

**Table 2.4.** **Variation of the thiol content with the TGA concentration and different reaction temperature. Reaction conditions: PVA concentration, 2%; $H_2SO_4$ concentration, 1%; reaction time, 24 h.**

| **TGA conc. (%)** | **Thiol content at various temperature (mmol/g)** | | | |
|---|---|---|---|---|
| | **50 (°C)** | **60 (°C)** | **70 (°C)** | **80 (°C)** |
| 5 | 0.5 | 2.3 | 2.4 | 2.5 |
| 10 | 0.9 | 2.5 | 2.7 | 2.7 |
| 15 | 1.4 | 3.1 | 2.9 | 2.9 |
| 20 | 1.9 | 3.6 | 3.5 | 3.3 |
| 25 | 2.0 | 3.9 | 3.7 | 3.5 |

The equilibrium thiol content as a function of the reaction temperature is presented in Figure 2.6 and Table 2.5. Interestingly, a sharp break in the thiol content variation with the increasing temperature is observed at 60 °C. As the reaction temperature increases at 60 °C, the thiol content enhanced from 2.0 to 3.9 mmol/g and beyond this temperature thiol content decreased due to the in-situ interaction between hydroxyl groups of PVA. At higher temperature, these –OH groups would not react with carboxyl group of acid.

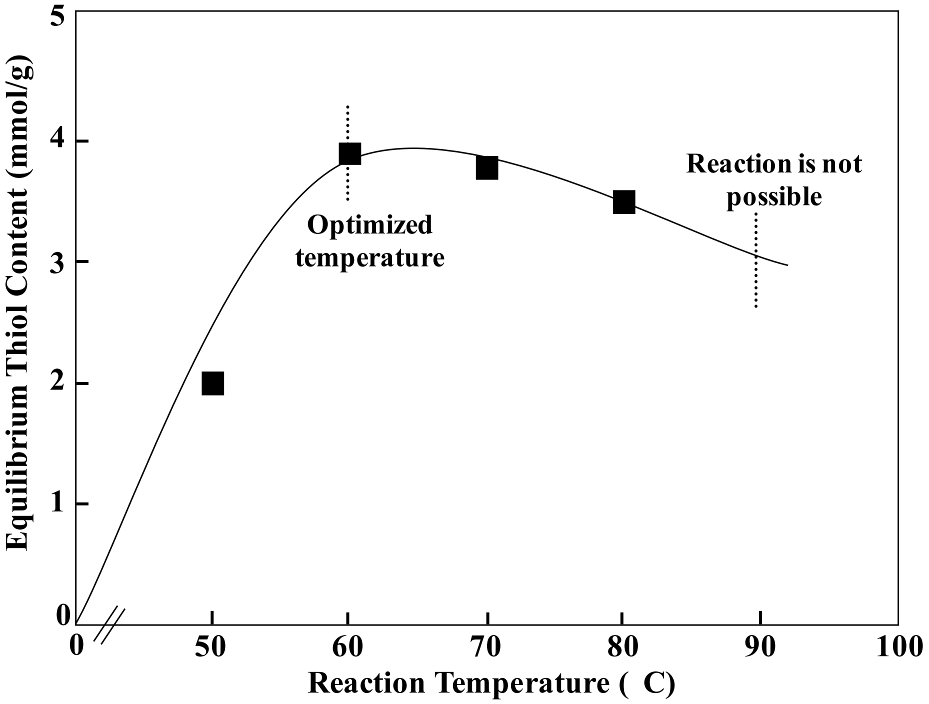

**Figure 2.6. Variation of the thiol content with the reaction temperature. Reaction conditions: PVA concentration, 2%; TGA concentration, 25%; $H_2SO_4$ concentration, 1%; reaction time, 24 h.**

**Table 2.5. Variation of the thiol content with the reaction temperature. Reaction conditions: PVA concentration, 2%; TGA concentration, 25%; $H_2SO_4$ concentration, 1%; reaction time, 24 h.**

| Temperature (°C) | Thiol Content (mmol/g) |
|---|---|
| 50 | 2.0 |
| 60 | 3.9 |
| 70 | 3.6 |
| 80 | 3.5 |

This result was probably due to the fact that the reactants did not have the enough activation energy to react at such a low temperature. It indicates that the optimized reaction temperature at 60 °C for PVA esterification with TGA. Our observations are quite in line with other workers that PVA modification at higher temperature did not improve the result [36].

### 2.3.5. Influence of the Catalyst Concentration

In esterification reaction, catalyst plays very important role in reaction acceleration. A catalyst performance indicates the progress of the reaction in the shortest time with good yield and makes the process cost effective. Due to the presence of a catalyst, it lowers down the activation energy of esterification reaction as compared to the without catalysed reaction. The effect of catalyst concentration on the thiol content in acid-alcohol mixture is investigated in Figure 2.7 and Table 2.6.

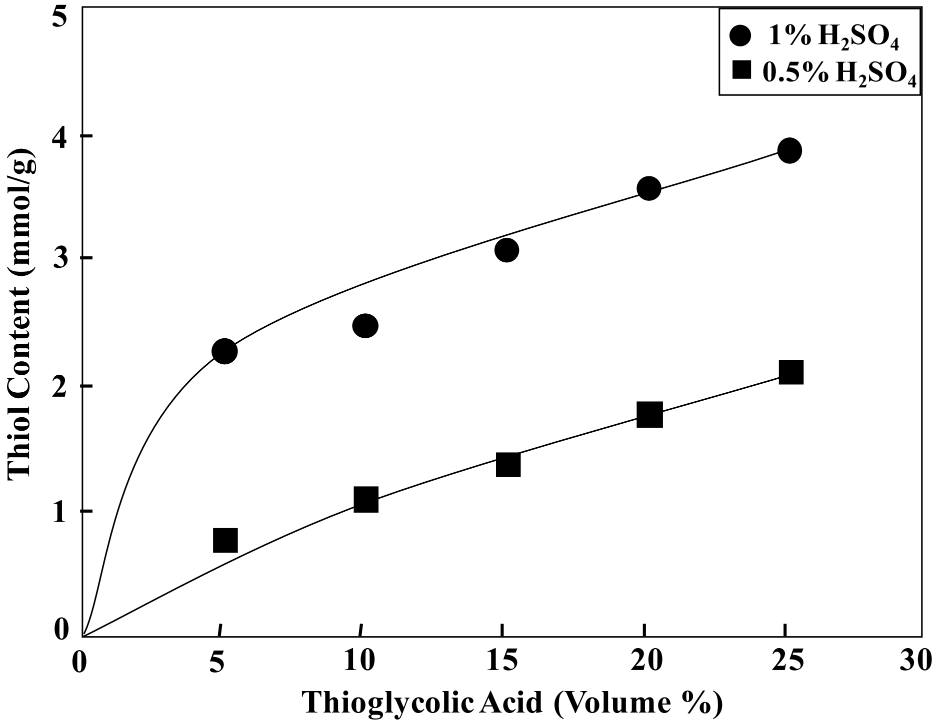

**Figure 2.7. Variation of the thiol content with the TGA concentration at catalyst concentrations. Reaction conditions: PVA concentration, 2%; TGA concentration, 25%; reaction temperature, 60 °C; reaction time, 24 h.**

**Table 2.6. Variation of the thiol content with the TGA concentration at catalyst concentrations. Reaction conditions: PVA concentration, 2%; TGA concentration, 25%; reaction temperature, 60 °C; reaction time, 24 h**

| TGA conc. (%) | Thiol content at various catalyst concentration | |
|---|---|---|
| | 0.5 (%) | 1 (%) |
| 5 | 0.8 | 2.3 |
| 10 | 1.1 | 2.5 |
| 15 | 1.4 | 3.1 |
| 20 | 1.9 | 3.6 |
| 25 | 2.1 | 3.9 |

In the presence of catalyst TGA is enough to initiate to react with the vinyl –OH group of PVA and bind –SH group into the matrix. As the catalyst, concentration increases from 0.5 to 2%, the thiol content showed an increasing trend. With the increase in catalyst amount from 0.5 to 1%, the ester formation increases this is due to the availability of large surface area and acid sites, which favors the dispersion of more active species. Therefore, the accessibility of the large number of molecules of the reactants to the catalyst surface is favored [37]. Previous studies showed that the minimum amount of catalyst is enough to initiate this process [30], therefore 1% $H_2SO_4$ concentration is optimized with respect to acid concentration keeping all other parameters constant from subsequent experiments.

### 2.3.6. Swelling Studies

Pure PVA films become water soluble due to the high hydrophilic nature of the polymer. Due to the presence of a large number of –OH groups in the PVA matrix which supports in the extensive formation of hydrogen bonding. TGA being a bifunctional acid (having two functional groups SH and COOH) may react with the –OH groups of PVA chains and this result favored in the formation of both intermolecular and intramolecular type of ester linkages among them. In this process, PVA was reacted with TGA at an optimized concentration with the varied reaction temperature from 50 to 80 °C. The observation of swelling studies of temperature regulated TPVA samples is presented in Figure 2.8 and Table 2.7.

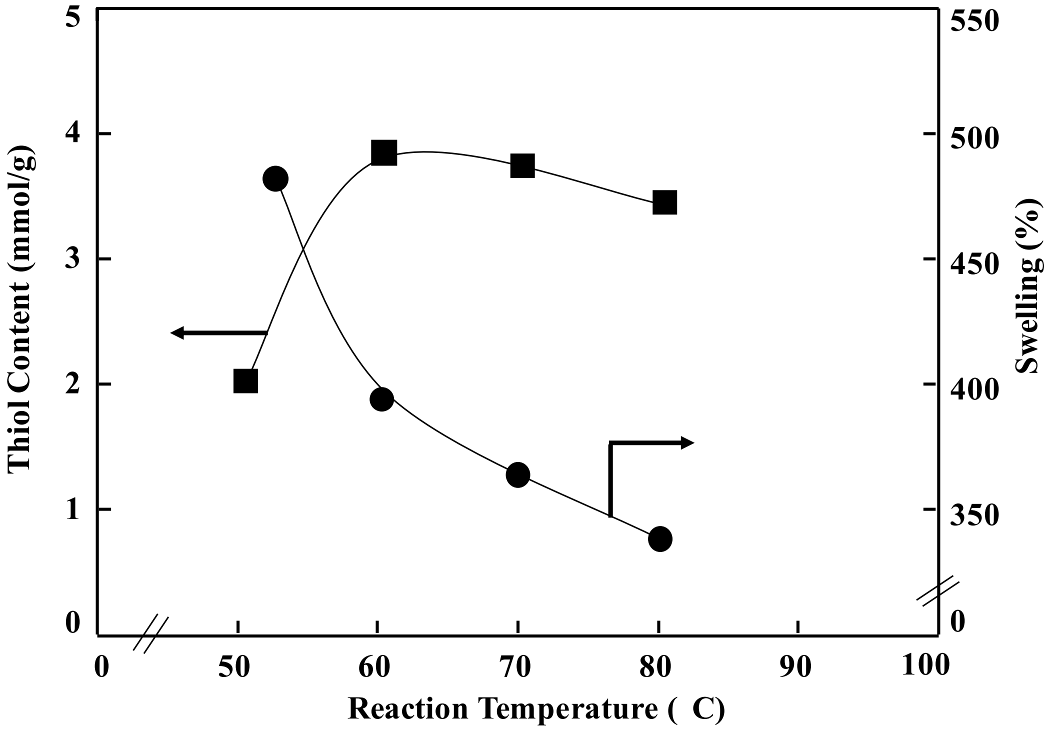

**Figure 2.8. Variation of the thiol content and the swelling with the reaction temperature. Conditions: PVA, 2%; TGA, 25%; $H_2SO_4$, 1%; reaction time, 24 h; swelling temperature, 40 °C; swelling time, 24 h**

**Table 2.7. Variation of the thiol content and swelling with the reaction temperature. Conditions: PVA, 2%; TGA, 25%; $H_2SO_4$, 1%; reaction time, 24 h; swelling temperature, 40 °C; swelling time, 24 h**

| Reaction Temperature (°C) | Thiol Content (mmol/g) | Swelling (%) |
|---|---|---|
| 50 | 2.0 | 487 |
| 60 | 3.9 | 398 |
| 70 | 3.6 | 364 |
| 80 | 3.5 | 340 |

The swelling behavior of different TPVA samples was studied at 40 °C for 24 h. After esterification, PVA structure become rigid, free voids become lesser and this inhibits the free movement of water molecules in polymeric chain. The TPVA was found good swelling property without any dissolution of the PVA.

The schematic presentation of the esterification process at different temperature is shown in Figure 2.9. As the reaction temperature increases from 50 to 80 °C, the resulting thiol content shows negligible decreasing trend with a noticeable decrease in the swelling of same TPVA samples.

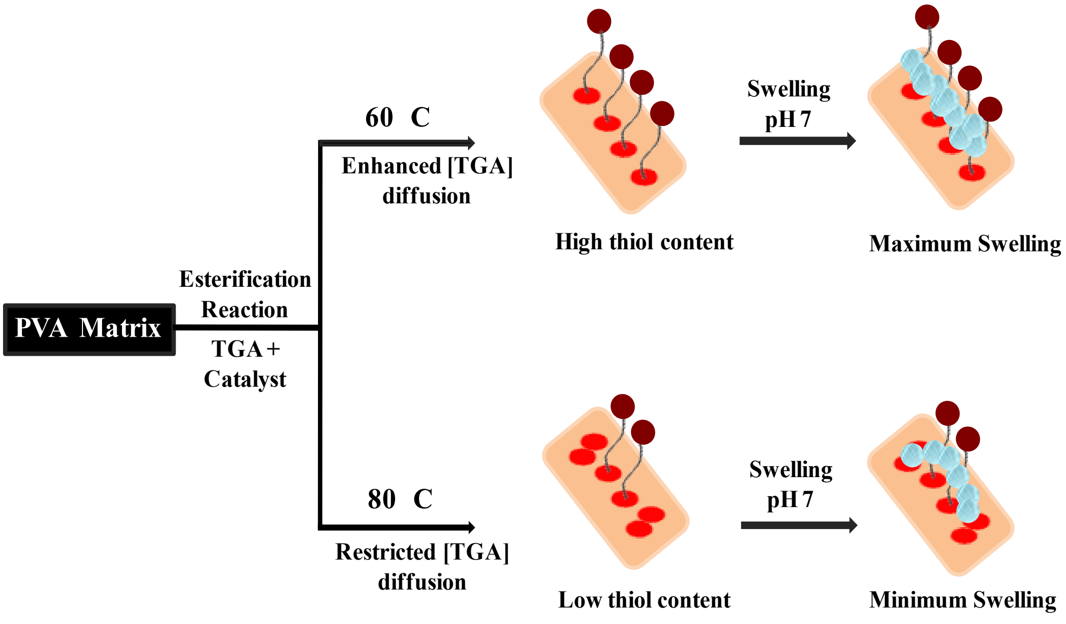

**Figure 2.9. The schematic presentation of the esterification process at different reaction temperature. ● OH group, ● SH group, ● $H_2O$**

The higher reaction temperature, more –OH groups undergo condensation with each other leading to the loss of the reactive sites and inhibit the TGA diffusion in the matrix. Moreover this process leads to a crosslinked structure where chain mobility is diminished. The cumulative effect of the lower esterification and crosslinking leads to lower water uptake in the matrix prepared at 80°C.

### 2.3.7. ATR-IR Studies

The ATR-IR spectra in absorbance of virgin PVA and thiolated PVA samples are shown in Figure 2.10 and table 2.8. The selected PVA has a degree of hydrolysis of 85-90%. The very strong band observed from 3200 to 3500 $cm^{-1}$ may be assigned to OH stretching due to the strong hydrogen bond of intramolecular and intermolecular type [38-40]. The CH stretching vibration was observed at 2934 and 2904 $cm^{-1}$ [41]. The peaks at 1712 and 1081 $cm^{-1}$ may be attributed to the stretching vibration of C=O and C–O of the remaining unhydrolyzed vinyl acetate group of the PVA [38]. The peak at 1374 $cm^{-1}$ is due to $–CH_2–$ wagging and that at 1323 $cm^{-1}$ is due to CH and OH bending [42].

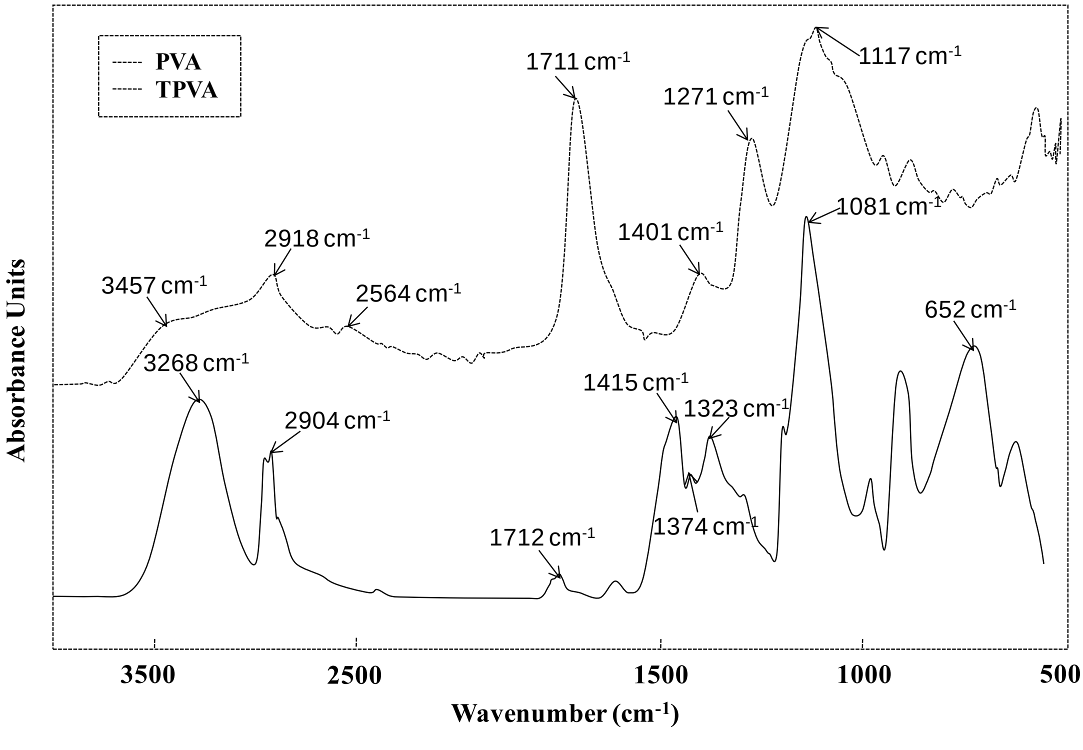

**Figure 2.10. ATR-IR spectra of pure PVA and thiolated PVA films**

In the IR spectrum of thioglycolic acid treated PVA film, the interaction of PVA with TGA results in the formation of ester owing to intermolecular or intramolecular cross-linking of the chains having the expected structure as shown in above figure. After esterification the shape and intensity of peaks at 3457 $cm^{-1}$ get change due the absence of free OH group in the matrix. The stretching band has submerged the band of the ester carbonyl and a sharp intense peak is observed at 1711 cm$^{-1}$ for C═O stretching due to the involvement of more groups in the matrix. A weak peak appears at 2564 cm$^{-1}$ indicates the presence of thiol group in the matrix after esterification of PVA [38]. These results indicate that the thiolation process has indeed taken place.

**Table 2.8. Peaks description of ATR-FTIR spectra of pure PVA and TPVA samples**

| **Groups** | **Wavenumber (cm$^{-1}$)** |
|---|---|
| OH stretching | 3200 to 3500 |
| CH stretching vibration | 2934 and 2904 |
| stretching vibration of C=O and C–O | 1712 and 1081 cm$^{-1}$ |
| –$CH_2$– wagging | 1374 |
| CH and OH bending | 1323 |
| SH | 2564 |

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# Chapter 3

# CROSSLINKING STUDIES OF THIOLATED POLYVINYLALCOHOL (TPVA)

## 3.1. Introduction

With the development of new facilities and materials, people benefit from the new technologies to lead a much more comfortable life. However, there are some unexpected damages, of the environment which have become serious issues interrupted our normal life. It is quite important to develop materials which not only provide the convenience for the human life, but also minimize the negative impact to the environment after being used. Large variety of biodegradable polymers is used frequently in commodity materials but they suffer from insufficient properties for applications, such as poor chemical stability, relatively high cost. Therefore, there is a strong need to find an alternative to the biodegradable polymer to improve the properties of existing polymers.

Polyvinyl alcohol (PVA) has acquired special attention because of its good transparency, luster, antielectrostatic properties, chemical resistance and toughness. PVA is a water soluble biocompatible polymer and is largely used as fiber (vinylon), film, in the paper industry, in textile sizing, as a modifier of thermosetting resins, in plywood manufacture, as pressure-sensitive adhesives and emulsifier [1-4]. The final properties of PVA mainly depend on the properties of its parent polymer, i.e. poly(vinyl acetate), its polymerization conditions and degree of hydrolysis. Due to its readily soluble nature and low solubility in organic solvent, PVA shows very limited reference in different scope of science and technology.

Crosslinking is a vital tool for the modification of existing PVA through its hydroxyl groups and opens up a new domain of applications of this material. The stability of crosslinked PVA in highly acidic or highly alkaline environments has been demonstrated [5]. While, the literature on applications as membranes or support material in water treatment is spasmodic [6,7], there has been a continuing effort in the biotechnology to use PVA membranes for protein recovery [8,9]. Crosslinked PVA gels have been studied extensively as biomaterials for artificial kidney and pancreas, glucose sensors, immuno-isolation membranes, artificial cartilage, contact lenses and drug delivery systems [10].

One of the unfortunate properties of PVA, however, is its tendency to become crosslinked by a number of chemical species, aldehydes, acids, borate, perborate, inorganic ligands and dyes. Wang *et al* were observed the formation of glutaraldehyde crosslinked CS-PVA based semi-interpenetrating pH sensitive hydrogel [11]. In further studies, the glutaraldehyde was reported for the mild crosslinking of PVA in order to fabricate polymer matrices for entrapment of [2]. Basiuk *et al* studied the new method of preparation glutaraldehyde crosslinked composites of PVA with carbon nanotubes (CNTs) [12]. Recently, the crosslinking of biodegradable blend films of PVA and gelatin were studied with glutaraldehyde by forming acetal linkage between adjacent macromolecules of gelatin and PVA [13].

The PVA crosslinking with divinyl sulphone under alkaline conditions at 70°C has been reported [14]. In another study [15] boric acid crosslinked PVA beads were used for cell immobilization. Sodium sulfate was utilized as an inducer for crosslinking of PVA for fabricating microorganism-enclosing PVA hydrogel beads [16]. Atta *et al* prepared the temperature depending crosslinked PVA-MA-NIPAAm copolymers by using methylene bisacrylamide as crosslinker [17]. The crosslinking reaction of PVA with hexamethylene diisocyanate has been investigated recently [18]. Thus, crosslinking of the PVA may be achieved by the reaction of hydroxyl groups along with the polymer chain with diisocyanates to give urethane as a crosslinker. Wan *et al* reported the high loaded porous crosslinked poly(vinyl alcohol) resins [19].

Studies have been made of crosslinking PVA with the dicarboxylic acid oxalic, malonic and citric acid with sulfuric acid as catalyst at 90–120°C [20]. The crosslinking of PVA with maleic anhydride in the presence of sulphuric acid (catalyst) has been reported [21]. PVA has also been crosslinked with γ-glycidoxy-propyltrimethoxysilane to produce PVA-silica hybrid membranes, with the aim of improving both permeability and selectivity in matrix [22]. Jianqi *et al* reported thermo-crosslinked PVA/PAA hydrogel fiber for good temperature and pH sensitivity [23]. Jin *et al*, reported the pH responsive bi-component hydrogels in the form of fibrous membrane by heat treatment at 120 and 140 °C for 5 min [24]. Gohil *et al*, studied crosslinking of PVA using maleic acid as the crosslinker and the variation of curing temperature and reaction time [25]. The surface crosslinked thermoplastic starch (TPS)/PVA blend films were prepared by applying ultra violet (UV) irradiation [26]. Fully hydrolysed PVA samples have been crosslinked by heating over the range of 120–175 °C for 30–80 min for RO membranes [27]. PVA has been used to prepare membranes that have been crosslinked with excess formaldehyde in a water bath at room temperature for 20 h, and then heat treated [28].

A further point worth considering is the toxicity of the reagents or the by-products formed during the crosslinking. However, traditional methods of crosslinking suffer from several disadvantages, such as lack of precise control over crosslinking, toxic effect of the crosslinker. This applies particularly to formaldehyde, which in the presence of hydrochloric acid can form chloromethyl ether, the use of which is highly restricted as it poses a significant hazard. Therefore, there is a necessity to use eco-friendly crosslinker which inhibits the lethal effect. In our previous section in (Chapter 1), we optimized esterification parameters including reaction time, reaction temperature and reactant concentrations. In the present chapter, we have investigated the crosslinking of thiolated PVA with different crosslinkers at varying conditions, crosslinker nature, crosslinker content and crosslinking time. The crosslinking reaction occurred through the hydroxyl groups of the PVA and the carboxyl group of TGA and led to ester linkages. The coupling agents for crosslinking PVA, were sodiumtrimetaphosphate (STMP), boric acid (BA) and glyoxal (GLY).

STMP has been reported to be an effective crosslinking agent for various polymers in Figure 3.1 [29-31]. STMP is a salt of low toxicity having no adverse effects on humans. Dulong *et al*, reported STMP as a crosslinker for hyaluronan in the presence of sodium hydroxide and sodium chloride of different crosslinking densities [32]. Guar gum was also crosslinked using STMP for applications in colon-specific drug delivery [33]. The Crosslinking of anionic starch microspheres with STMP was studied through emulsification-crosslinking reaction [34]. Chaouat *et al* designed a simple process for PVA crosslinking with STMP to form membrane devices suitable for vascular grafts [35].

BA is very well known crosslinker in Figure 3.1 for PVA by the formation of borate linkage with a respective hydroxyl group of PVA. Miyazaki *et al,* investigated the role of boric acid as a crosslinker for a PVA film when the film is immersed in a boric acid aqueous solution [36]. In a recent study researcher observed the effect of boric acid treatment on PVA/Iodine polarizing films therefore, boric acid was believed to stabilize the PVA/Iodine complexes through crosslinking [37]. Liang *et al* concluded the selective crosslinking of both CS and PVA in a single step process by using respective crosslinker for each polymer. STMP and boric acid used as selective crosslinker for CS and PVA respectively [38].

GLY has been the most promising aldehyde used as a crosslinker in Figure 3.1 [39,40] and has been investigated the preparation of glyoxal crosslinked

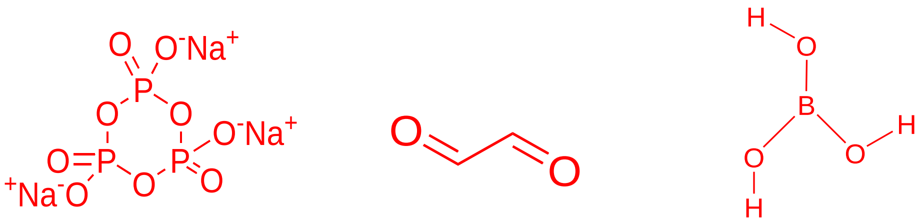
PVA/Pullulan blend films. The resulting crosslinked films were homogeneous and had higher tensile strengths and moduli than the simple blend. Zhang *et al* investigated PVA crosslinking with glyoxal via formation of acetal bonds between hydroxyl and an aldehyde group of respective components [41]. Blanes *et al* investigated the influence of glyoxal on the physical properties of glyoxal crosslinked PVA nanofibers. Resulting nanofibers showed smooth surface, amorphous in nature and colourless in appearance [42].

Therefore, in this section we report the comparative data of all crosslinkers in terms thiol content and swelling studies. Thiol content and swelling behaviour of crosslinked thiolated PVA were observed in terms of the effect of nature of crosslinker, crosslinker content, crosslinking time, and pH media.

## 3.2. Experimental

### 3.2.1. Materials

PVA (Mw. 1,50,000 and the degree of hydrolysis 85%) was supplied from Sigma. TGA, sodium hydroxide, sulfuric acid, glyoxal (GLY) and methanol (HPLC grade) were purchased from Merck, India. Sodiumtrimetaphosphate (STMP) was supplied from Sigma and boric acid (BA) was supplied from S D Fine Chemicals. All were used without further preparation. Ultra-pure water, resistivity less than 18 MΩcm, produced by a Millipore Milli-Q system was used throughout the experimental work.



(a) (b) (c)

**Figure 3.1. Structure of different crosslinkers (a) STMP (b) GLY and (c) BA**

### 3.2.2. Esterification of PVA

Homogenous solution of 2% PVA was prepared by dissolving 2 g PVA powder in 100 ml water under vigorous stirring for overnight at room temperature. Esterification reaction was carried out as reported previously (discussed in Chapter 2) under optimized parameters of 25% TGA concentration, reaction time 24 h, reaction temperature 60 °C and catalyst concentration of 1%. The thiol content of TPVA samples was 3.9 mmol/g and was used for subsequent crosslinking reaction in this study.

### 3.2.3 Crosslinking of Thiolated PVA (TPVA)

The TPVA solution further subjected to the crosslinking reaction with three crosslinkers of different nature, viz. STMP, BA and GLY. Varying concentration of crosslinkers from (0.05 to 1%) with respect to PVA concentration has been studied with increasing crosslinking time from (15 min to 1 h) at reaction temperature 60 °C. After completion of the reaction, the mixture was slowly poured into 12 M sodium hydroxide solution at pH 12, following into formation of white precipitate which was washed repeatedly with water and methanol, and dried in vacuum oven at room temperature.

### 3.2.4. Thiol Content Estimation

The amount of the involved and accessible thiol groups was successfully determined according to a protocol based on the *Volhard's silver nitrate method* [43]. The determination is based on the chemical affinity of silver by thiol groups. Following the protocol, 50 mg of dried TPVA has immersed in 50 ml of 0.01 M silver nitrate solution. The flasks were covered to avoid exposure to light and stirred in a shaker for 3 h prior to testing. The remaining silver nitrate was titrated with standardized 0.01 M potassium thiocyanate (KSCN) using iron ammonium sulfate hexahydrate as an indicator. The endpoint was detected when an excess of thiocyanate anion formed a red colored complex with the iron compound. The thiol content was expressed in mmol/g of polymer. In all cases, the tests were carried out in triplicate measurement.

### 3.2.5. Swelling Studies

The swelling studies of the crosslinked TPVA were carried out by measuring the amount of water incorporated into the sample. Pre-dried sample was immersed in milliQ water having a different pH at temperature 40 °C. The sample was taken out from water at certain time intervals and weighed after blotting out the excess of water from the surface of sample with tissue paper. They were put back in water immediately after weighing. The swelling behaviour of the sample was specified by a function of the times and the weight was recorded as a gram of water uptake per minute. After 24 h the equilibrium state is also determined at water uptake during the time reach steady state. The water absorption of the sample was calculated as the percent swelling by following equation [44]:

$$\text{Swelling (\%)} = \frac{Ws - W_d}{W_d} \times 100 \qquad \textit{eq. 1}$$

Where, $W_s$ and $W_d$ are the weight of the samples in the swollen and dry states, respectively.

### 3.2.6. Attenuated Total Reflectance Infrared Spectroscopy (ATR-IR)

The ATR-IR spectra of samples were recorded on Bruker Alpha P(Opus 65) spectrophotometer. The spectra of different crosslinked TPVA samples were recorded over the 400 - 4500 $cm^{-1}$ range.

## 3.3. Results and Discussion

Crosslinking is an adaptable path for improving the water resistance property in hydrophilic polymers. The crosslinking under different conditions leads to the formation of stable linkage in between different units of thiolated PVA. The schematic representation of the crosslinking process of thiolated PVA is presented in Figure 3.2. The optimization of the crosslinking parameters was carried out with three crosslinkers i.e. STMP, GLY and BA under specific conditions.

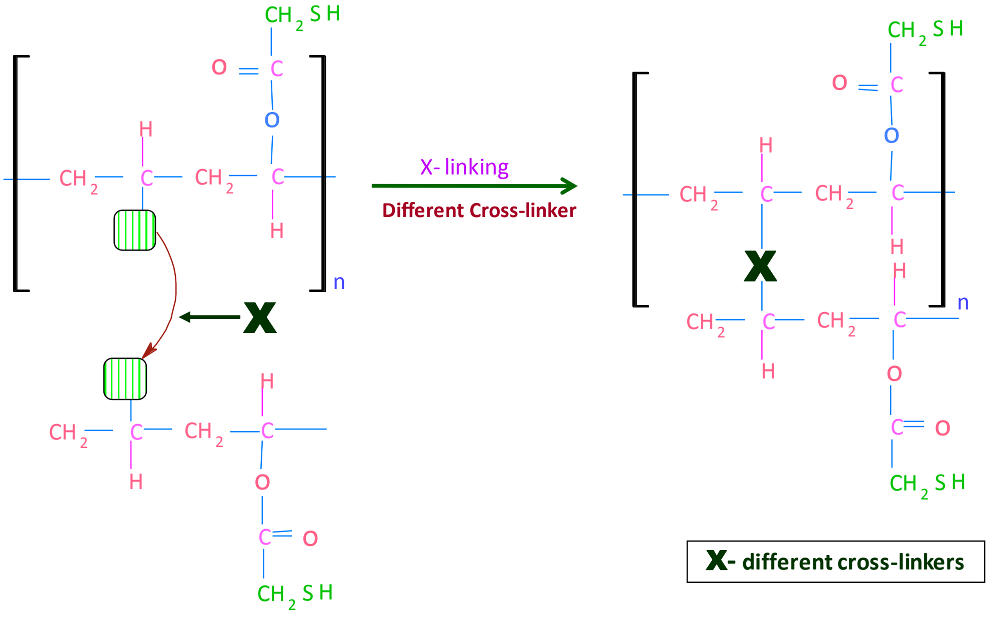


**Figure 3.2. Schematic representation of the crosslinking process of thiolated PVA**

All three crosslinker showed different bonding strategies and distinct properties with each other. The crosslinking studies of thiolated PVA were monitored by various parameters (a) effect of TGA concentration (b) effect of crosslinking time (c) effect of crosslinker content (d) effect of nature of crosslinker (e) effect of pH.

### 3.3.1. Influence of the TGA Concentration

The comparative investigation of the variation of thiol content and swelling with STMP crosslinked and non crosslinked TPVA are presented in Figure 3.3, 3.4 and Table 3.1.

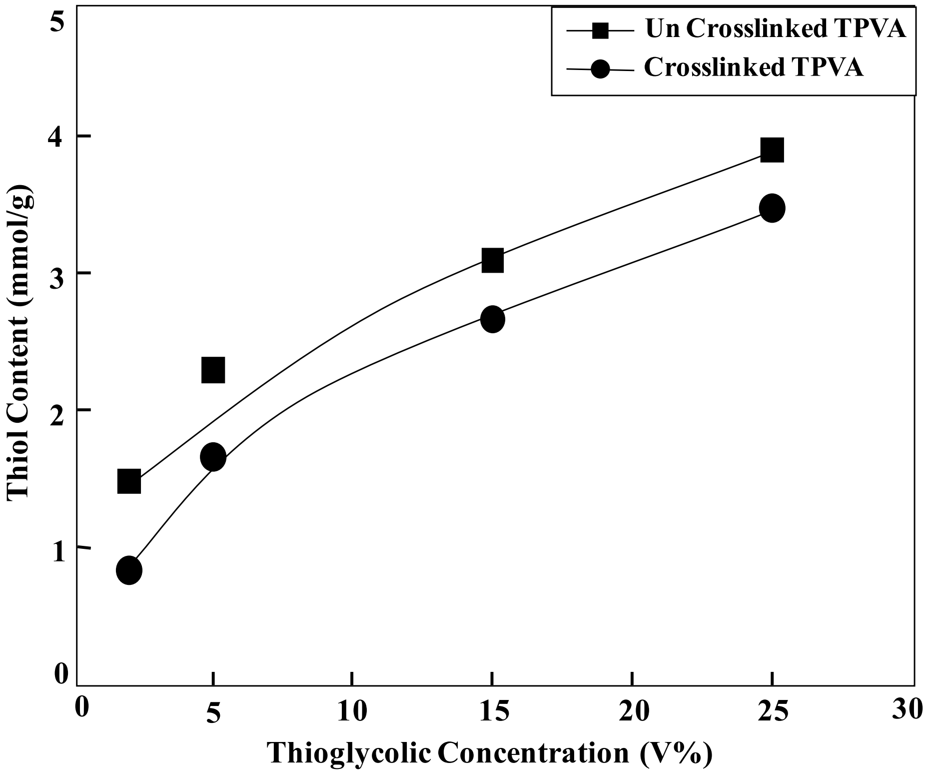


**Figure 3.3. Variation of the thiol content with the TGA concentration. Crosslinking conditions: Crosslinker, STMP; crosslinker content, 0.1%; crosslinking time, 30 min**

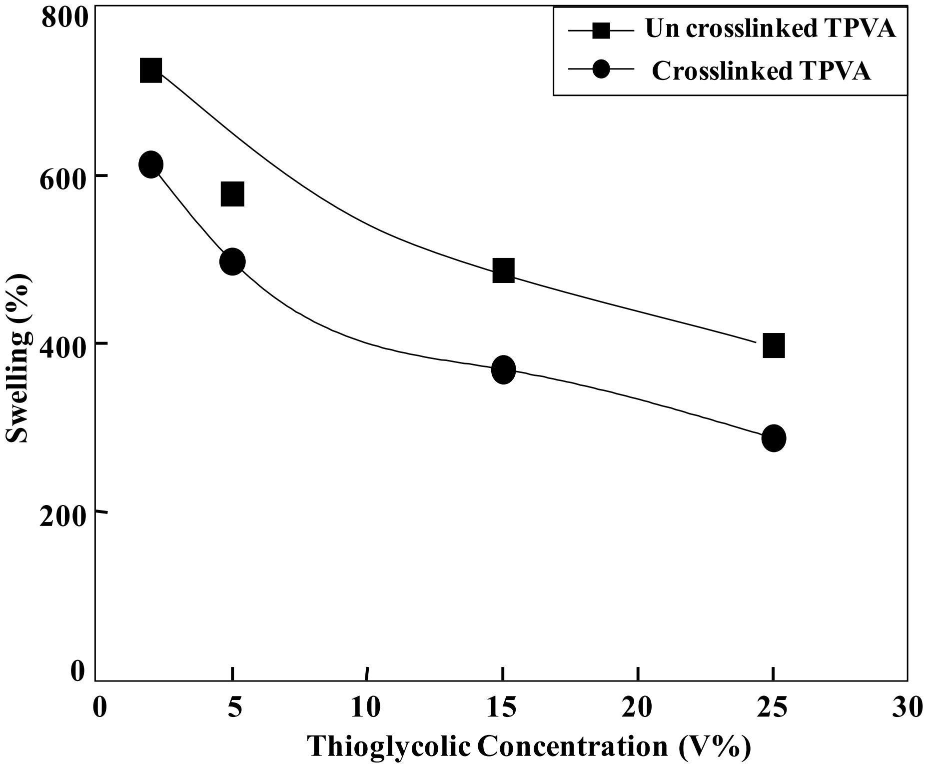


**Figure 3.4. Variation of the swelling with the TGA concentration. Crosslinking conditions: Crosslinker, STMP; crosslinker content, 0.1%; crosslinking time, 30 min**

**Table 3.1. Variation of the thiol content and swelling with the TGA concentration. Crosslinking conditions: Crosslinker, STMP; crosslinker content, 0.1%; crosslinking time, 30 min**

| TGA Concentration (v%) | Uncrosslinked TPVA | | Crosslinked TPVA | |
|---|---|---|---|---|
| | Thiol Content (mmol/g) | Swelling (%) | Thiol Content (mmol/g) | Swelling (%) |
| 2 | 1.5 | 724 | 0.84 | 613 |
| 5 | 2.3 | 578 | 1.67 | 498 |
| 15 | 3.1 | 487 | 2.67 | 369 |
| 20 | 3.9 | 398 | 3.48 | 287 |

In our study, the acid concentration variation was investigated from 5 to 25% with respect to PVA concentration and the STMP is used as crosslinker. As the TGA concentration increases, more hydroxyl groups of PVA get esterified and remaining hydroxyl groups were available for crosslinking. The reaction conditions were adjusted so that the resulting thiol content remains in the range of 0.5 to 4 mmol/g, so that we can monitor the influence of the both conditions on the physical structure of the PVA. As resultant, the crosslinked TPVA matrix become more hydrophobic.

### 3.3.2. Influence of the Nature of Crosslinkers

The variation of the thiol content with different crosslinkers is presented in Figure 3.5 and Table 3.2. Thiol content changes with the nature of the crosslinker due to different crosslinking strategy. It is evident that crosslinking leads to the development of structure were affection of thiol are inaccessible and hence this is reflected in the lower thiol content in crosslinked material. Certainly, the structural changes depend as the nature of the crosslinked and contribute to the variation in thiol content.

In case of GLY, the aldehyde groups form covalent acetal bonds with the –OH groups of PVA and the resonance established with adjacent double ethylenic bonds via a Schiff reaction [40,41]. Ionic crosslinking is a simple and mild procedure in contrast to covalent crosslinking. Both BA and STMP are suitable examples of ionic crosslinkers. BA has active four hydroxyl groups in each unit which interact with hydroxyl groups of PVA. It forms a stable borate linkage with an active hydroxyl group of thiolated PVA. While the STMP forms the phosphate linkage with hydroxyl group of thiolated PVA [38]. Thiol content decreases in case of GLY due to efficient crosslinking, therefore swelling ability and thiol content become diminished.

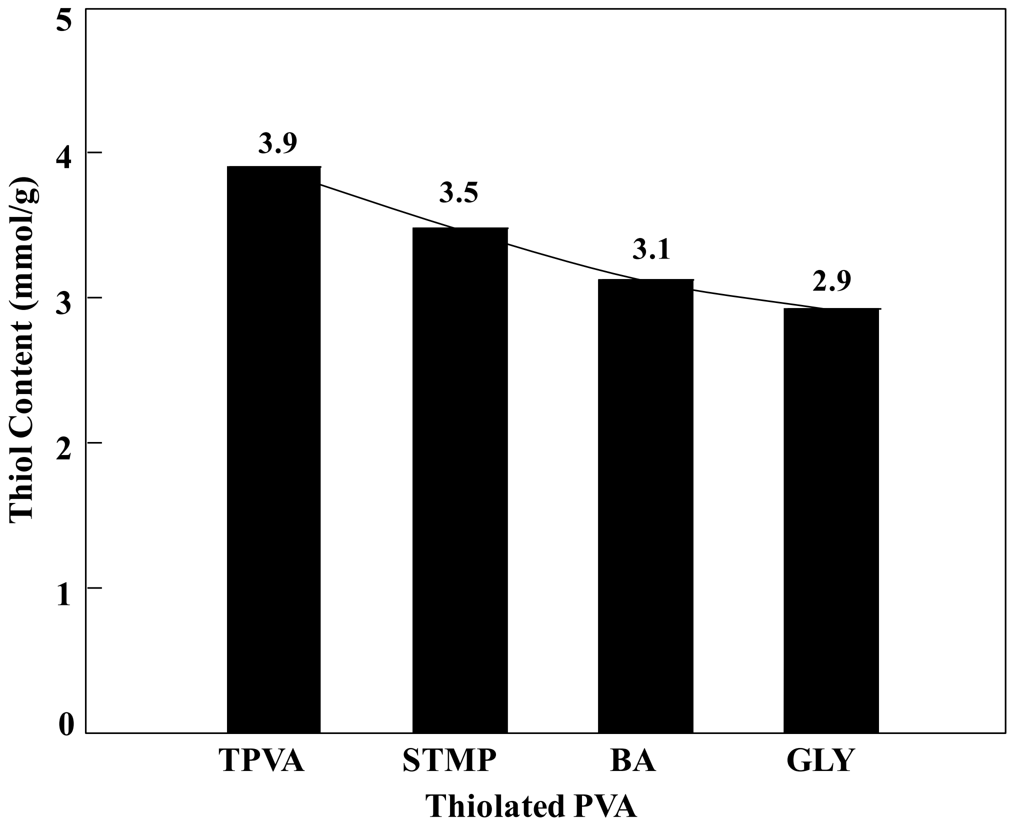


**Figure 3.5. Variation of the thiol content with the crosslinker nature. Crosslinking conditions: Crosslinker content, 0.1%; crosslinking time, 30 min**

**Table 3.2. Variation of the thiol content with the crosslinker nature. Crosslinking conditions: Crosslinker content, 0.1%; crosslinking time, 30 min**

| Samples | Thiol Content (mmol/g) |
|---|---|
| TPVA | 3.9 |
| STMP | 3.5 |
| BA | 3.1 |
| GLY | 2.9 |

The variation of the swelling with the different nature of the crosslinker is presented in Figure 3.6 and Table 3.3.

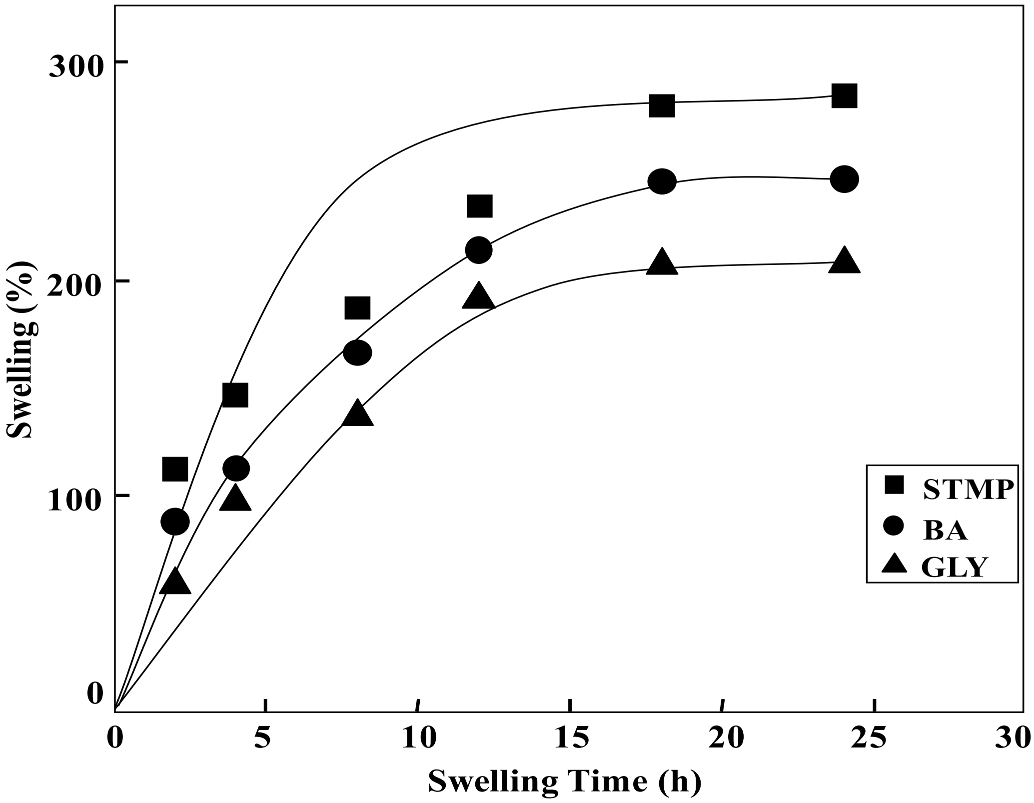


**Figure 3.6. Variation of the swelling with the time for different crosslinkers. Crosslinking conditions: Crosslinker content, 0.1%; crosslinking time, 30 min; swelling temp, 40 ºC; pH, 7**

**Table 3.3. Variation of the swelling with the time for different crosslinkers. Crosslinking conditions: Crosslinker content, 0.1%; crosslinking time, 30 min; swelling temp, 40 ºC; pH, 7**

| **Time (h)** | **Swelling (%)** | | |
|---|---|---|---|
| | **STMP** | **BA** | **GLY** |
| 2 | 112 | 87 | 58 |
| 4 | 147 | 108 | 97 |
| 8 | 188 | 167 | 136 |
| 12 | 235 | 215 | 192 |
| 18 | 282 | 247 | 206 |
| 24 | 287 | 248 | 208 |

It is important to mention that the crosslinker nature plays a prominent role in the physical properties of initial polymer. Results indicate the variation of swelling ability of TPVA with different crosslinkers at increasing of swelling time. It is observed that the swelling reaches equilibrium within 24 h for all crosslinker inspite of their chemical structure.

### 3.3.3. Influence of the Crosslinker Content

The crosslinking ability of polymer is greatly affected by the amount of crosslinker. The variation of the thiol content with the crosslinker content is presented in Figure 3.7 and Table 3.4.

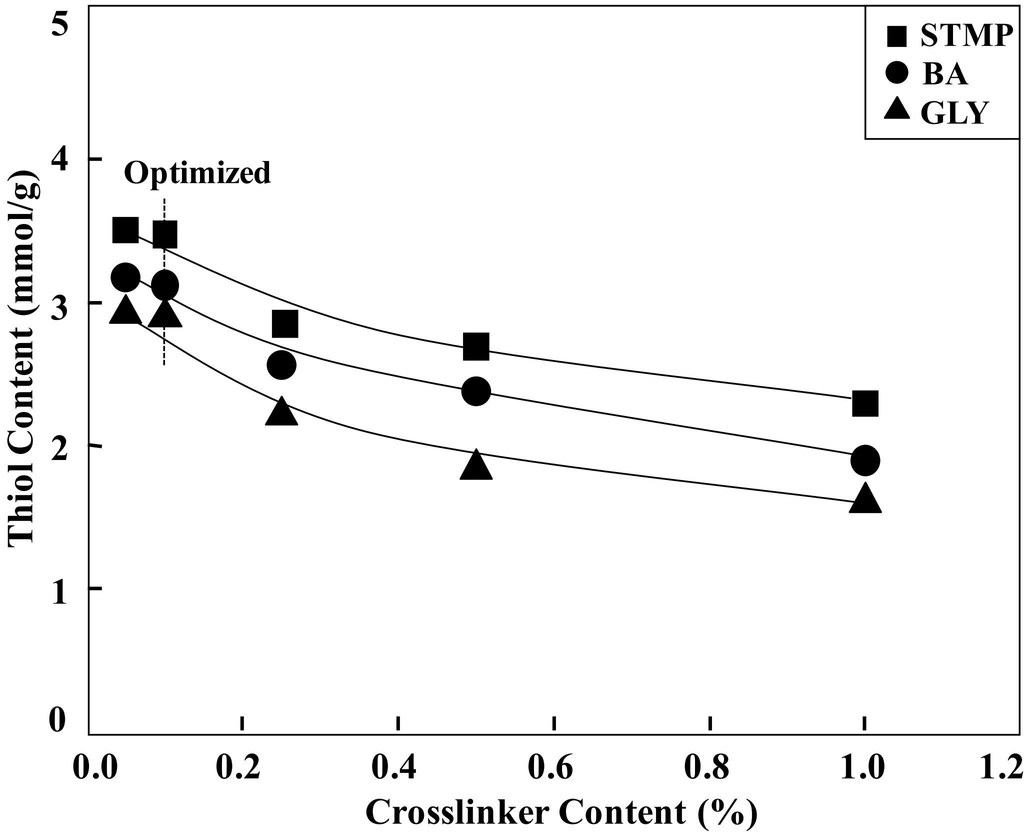


**Figure 3.7. Variation of the thiol content with the crosslinker content. Crosslinking conditions: Crosslinking time, 30 min**

As the crosslinker content increased, thiol content showed deceasing pattern similar to the swelling results. The few molecules of the crosslinker were not able to promote a suitable network to prevent polymer solubility in water. The addition of more crosslinker to the polymeric solution favored the reaction in different edges of the crosslinker molecule and reduced the free volume of the material, which improved the water resistance in the matrix.

**Table 3.4. Variation of the thiol content with the crosslinker content. Crosslinking conditions: Crosslinking time, 30 min**

| Crosslinker Content (%) | Thiol Content (mmol/g) | | |
|---|---|---|---|
| | STMP | BA | GLY |
| 0.05 | 3.5 | 3.2 | 2.9 |
| 0.10 | 3.5 | 3.1 | 2.9 |
| 0.25 | 2.8 | 2.5 | 2.2 |
| 0.50 | 2.6 | 2.4 | 1.9 |
| 1.0 | 1.9 | 1.9 | 1.7 |

The variation of the swelling with the crosslinker content is presented in Figure 3.8 and Table 3.5. Swelling of all samples was studied for different crosslinkers at varying content from 0.05 to 1% in buffered solution of pH 7 at equilibrium time of 24 h.

**Table 3.5. Variation of the percent swelling with the crosslinker content. Crosslinking conditions: Crosslinking time, 30 min; swelling time, 24 h; swelling temp, 40 ºC**

| Crosslinker Content (%) | Swelling (%) | | |
|---|---|---|---|
| | STMP | BA | GLY |
| 0.05 | 301 | 266 | 207 |
| 0.10 | 287 | 248 | 208 |
| 0.25 | 246 | 201 | 187 |
| 0.50 | 189 | 167 | 144 |
| 1.0 | 124 | 103 | 96 |

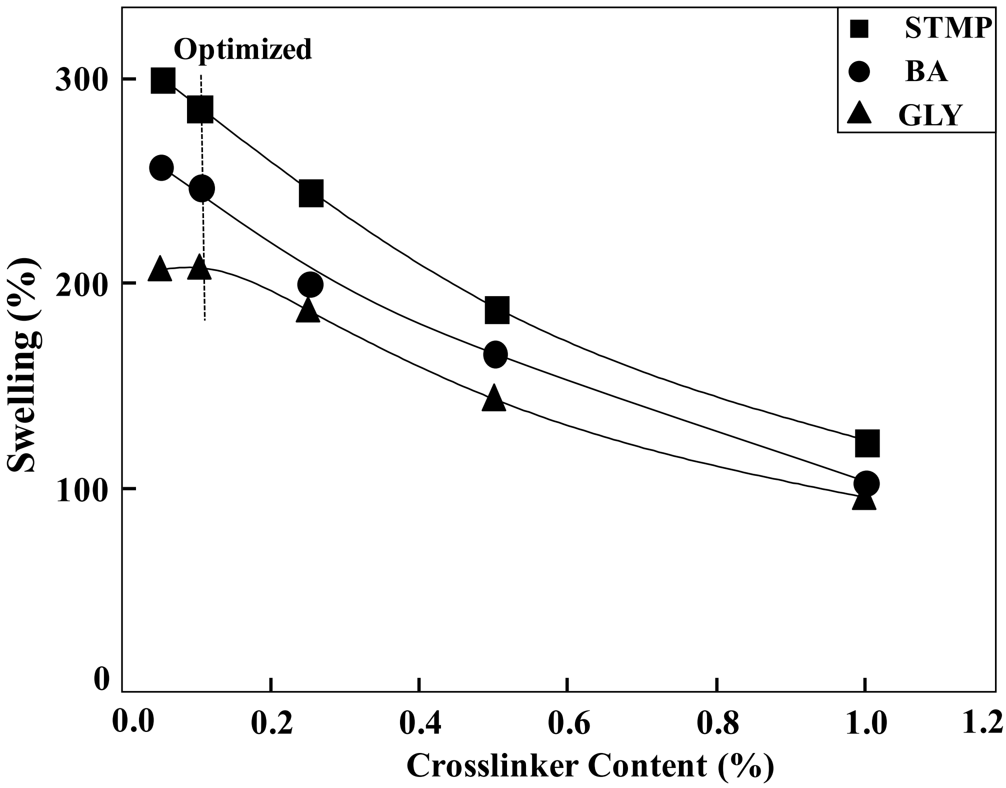


**Figure 3.8. Variation of the percent swelling with the crosslinker content. Crosslinking conditions: Crosslinking time, 30 min; swelling time, 24 h; swelling temp, 40 $^{o}$C**

It is conceivable that the increase in the amount of crosslinker leads to an increase in the crosslinking density of per unit volume, restricting the swelling behaviour of polymer [45]. Therefore, in our studies we use three different crosslinkers and report comparative data of each. In all three cases, at lower crosslinker content (0.05%), the unreacted PVA leached out from the matrix. Afterwards, when crosslinker content increases to 0.1%, it corresponds to appropriate amount of crosslinking agent for insolubility of the TPVA in all crosslinkers.

### 3.3.4. Influence of the Crosslinking Time

Crosslinking time also plays a well defined role in crosslinking. According to this study, more the crosslinking time higher is the crosslinking which is possible due to the maximum interaction of crosslinker with polymer, leading to increasing crosslinking density. The variation of the thiol content with the crosslinking time is presented in Figure 3.9 and Table 3.6. The graph showed that with increasing crosslinking time, the thiol content diminishes.

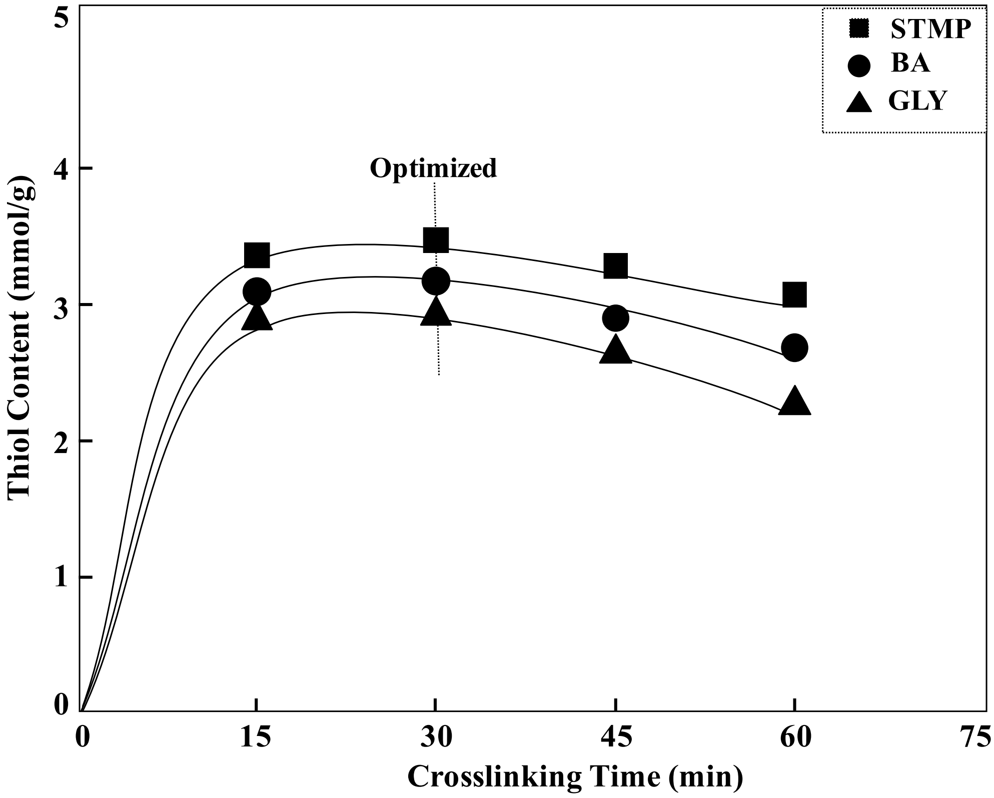


**Figure 3.9. Variation of the thiol content with the crosslinking time. Crosslinking conditions: Crosslinker content, 0.1%**

**Table 3.6. Variation of the thiol content with the crosslinking time. Crosslinking conditions: Crosslinker content, 0.1%**

| Crosslinking Time (min) | Thiol content (mmol/g) | | |
|---|---|---|---|
| | STMP | BA | GLY |
| 15 | 3.4 | 3.1 | 2.9 |
| 30 | 3.5 | 3.2 | 2.9 |
| 45 | 3.3 | 2.7 | 2.6 |
| 60 | 3.0 | 2.7 | 2.3 |

The variation of the swelling with the crosslinking time is presented in Figure 3.10 and Table 3.7. The similar effect is observed in swelling variation with crosslinking time for all crosslinker.

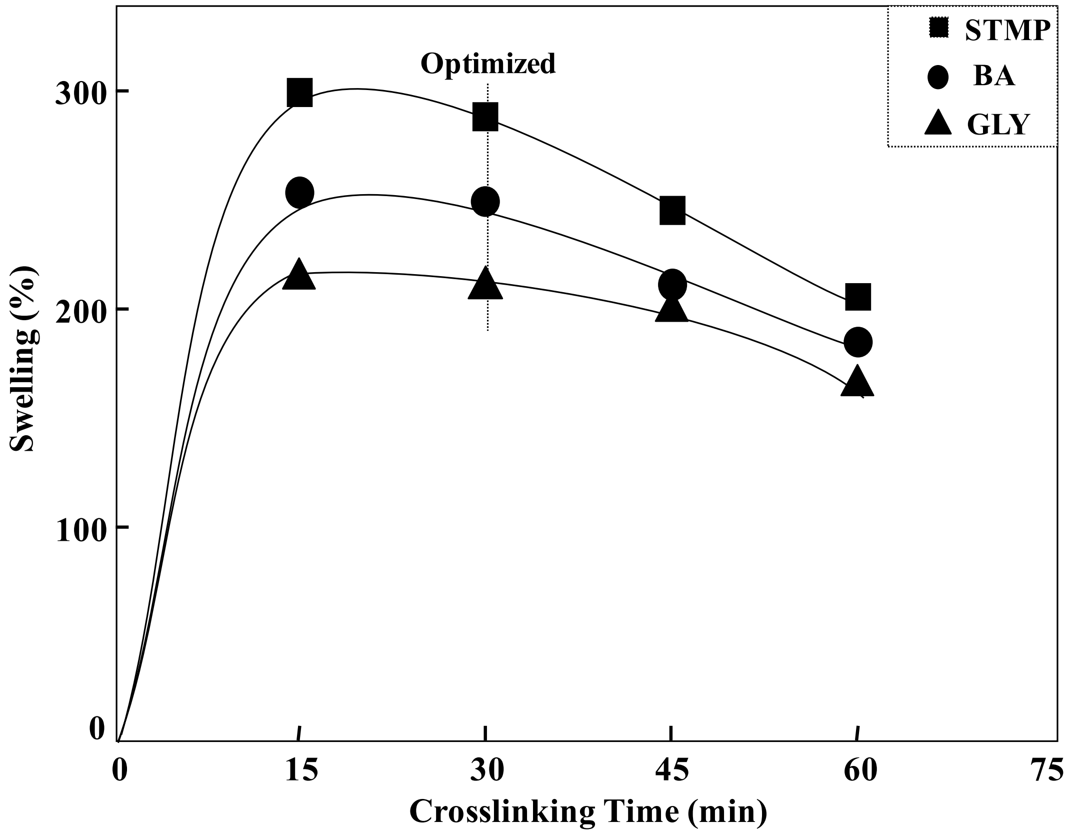


**Figure 3.10. Variation of the swelling with the crosslinking time. Reaction conditions: Crosslinker content, 0.1%; swelling time, 24 h; swelling temp, 40 ºC**

**Table 3.7. Variation of the swelling with the crosslinking time. Crosslinking conditions: Crosslinker content, 0.1%; swelling time, 24 h; swelling temp, 40 ºC**

| Crosslinking Time (min) | Swelling (%) | | |
|---|---|---|---|
| | STMP | BA | GLY |
| 15 | 298 | 259 | 213 |
| 30 | 287 | 248 | 208 |
| 45 | 243 | 210 | 198 |
| 60 | 207 | 183 | 164 |

The crosslinking density of GLY crosslinked thiolated PVA the crosslinking density is high as compared with other two ionically crosslinked thiolated PVA, is influenced by their reaction duration. Therefore, from the above conclusion, we optimized STMP is as a suitable crosslinker for thiolated PVA.

### 3.3.5. Influence of the pH

The role of pH on the extent of swelling of the polymer is of great importance. Since a change in pH of swelling media often causes a fluctuation in free volume accessible to penetrate water molecules, it affects swelling properties of the base polymer. The variation of swelling at a different pH media for varying immersion time is, presented in Figure 3.11 and Table 3.8.

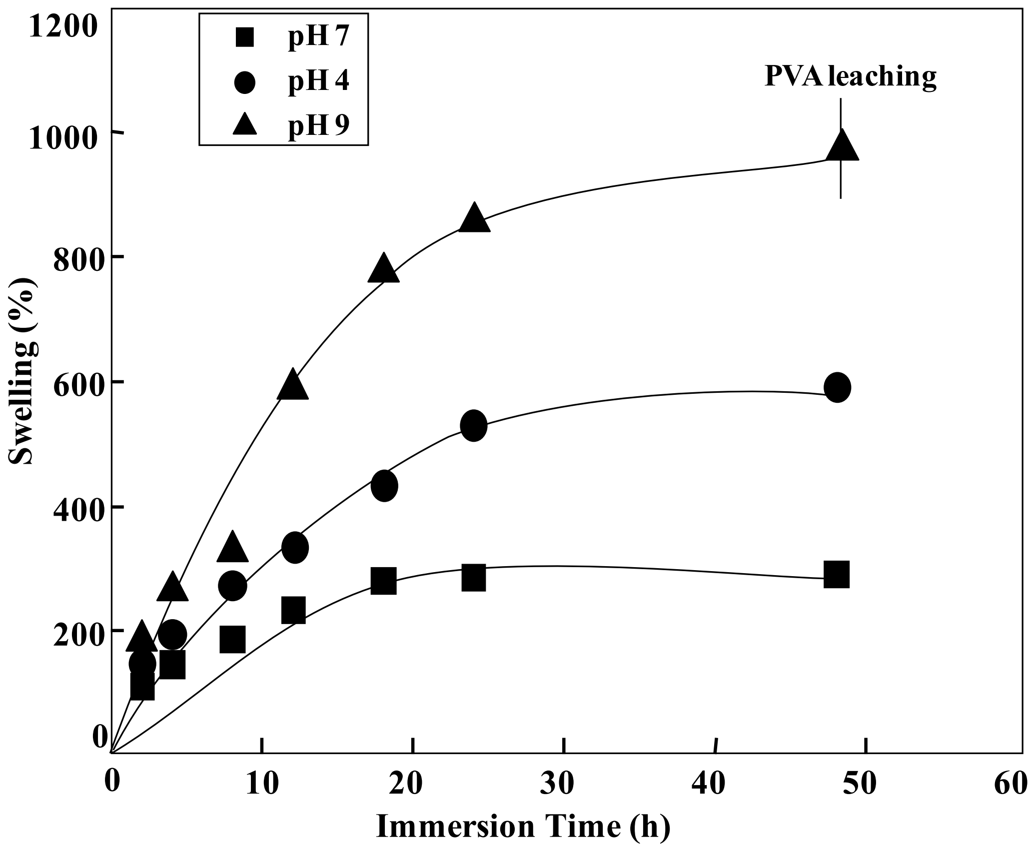


**Figure 3.11. Variation of the swelling with the different immersion time at varying pH. Crosslinking conditions: Crosslinker, STMP; crosslinker content, 0.1%; crosslinking time, 30 min; swelling temp, 40 °C**

In the present work, the equilibrium swelling behaviour of crosslinked thiolated PVA samples was investigated as a function of pH in the range of 4-9 at 40 °C. Swelling of crosslinked TPVA samples was found to increase in both acidic and basic medium and showed moderate value in neutral medium. The crosslinked sample was initially derived from the esterification reaction of PVA with TGA, and it is confirmed that the former derived crosslinked material is more pH sensitive. In acidic medium, the hydrolysis of ester takes place. Even the phosphate bond was weaker in basic medium due to this reason the swelling of TPVA in basic medium was not constant after 48 h.

**Table 3.8. Variation of the swelling with different immersion time at varying pH. Crosslinking conditions: Crosslinker, STMP; crosslinker content, 0.1%; crosslinking time, 30 min; swelling temp, 40 ºC**

| Swelling time (h) | Swelling (%) | | |
|---|---|---|---|
| | pH 4 | pH 7 | pH 9 |
| 2 | 148 | 112 | 186 |
| 4 | 196 | 147 | 265 |
| 8 | 227 | 188 | 329 |
| 12 | 286 | 235 | 588 |
| 18 | 322 | 282 | 776 |
| 24 | 418 | 287 | 857 |
| 48 | 446 | 287 | 974 |

Therefore, the pH 7 was optimized for further experiment at above other constant parameters. The water absorption capacity of the crosslinked TPVA was found to be greatly dependent on the pH of the surrounding medium.

### 3.3.6. ATR-IR Studies

ATR-IR spectra of uncrosslinked TPVA and crosslinked TPVA with different crosslinker are shown in Figure 3.12. In the spectrum of uncrosslinked TPVA, a broad band appears at 3457 cm$^{-1}$ due to the presence of hydroxyl groups in PVA. Absorption of asymmetrical stretching of C-H in the PVA backbone is appears at 2918 cm$^{-1}$. The two peaks at 1401 and 1271 cm$^{-1}$ are from the secondary O-H in-plane bending and C-H wagging vibrations. The band centered at 1030 cm$^{-1}$

represents the C-O stretching vibration of PVA. The sharp band appears at 1711 cm$^{-1}$ due to the presence of unhydrolyzed acetate groups from stock PVA and sharpness of peaks demonstrated the esterification of PVA [46]. Weak band appears at the 2564 cm$^{-1}$ is due the presence of thiol group in the polymer chain.

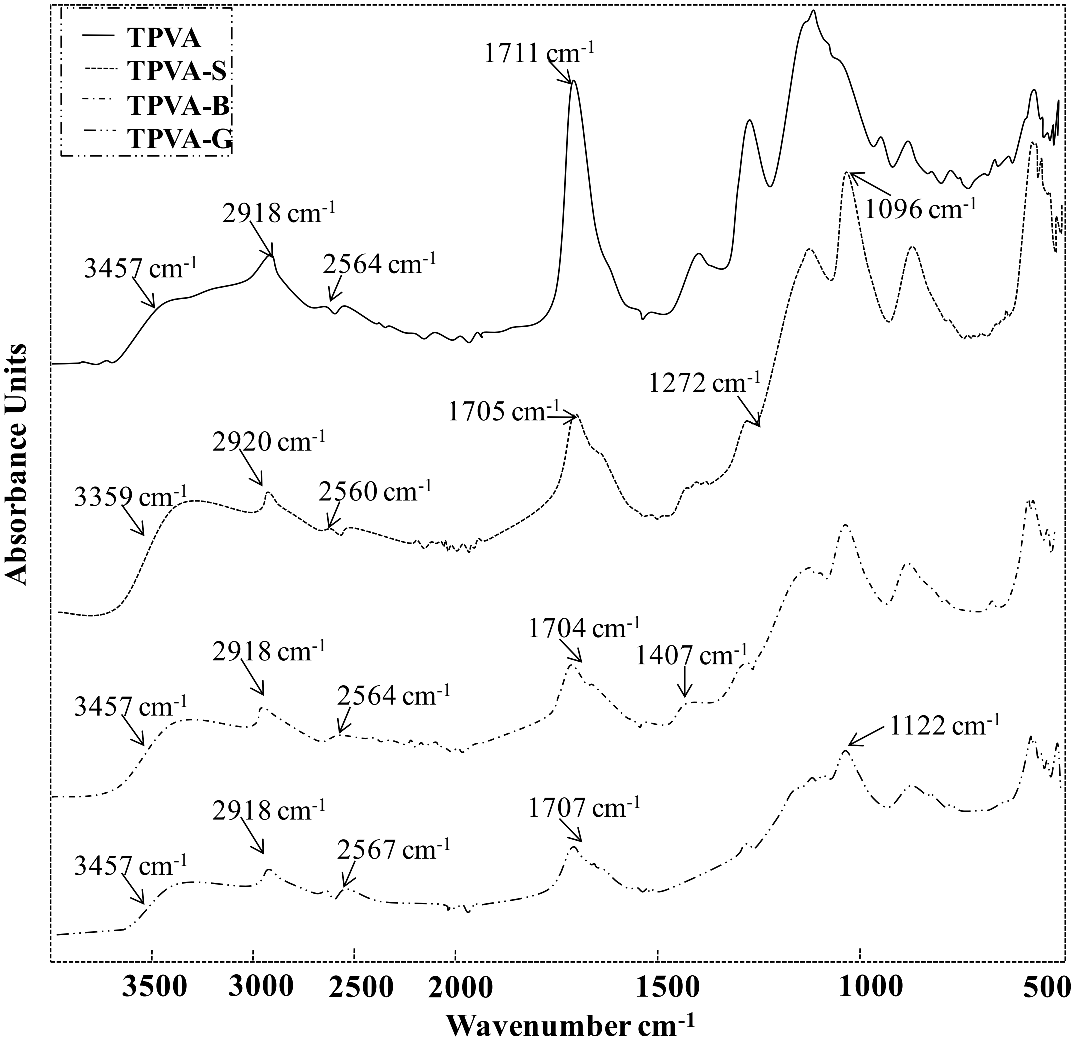


**Figure 3.12. ATR-IR spectra of uncrosslinked thiolated PVA and crosslinked thiolated PVA**

In STMP crosslinked TPVA, the band centered at 1272 cm$^{-1}$ and the shoulder at 1096 cm$^{-1}$ can be related to the stretching vibrations of pyrophosphate system P-O-P and P-O-H respectively [47]. The appearance of two bands in the spectrum of TPVA-S, confirm the ring opening of STMP and its subsequent binding to PVA chains, after crosslinking reaction. In GLY crosslinked TPVA, the C-C-C stretching band is presented at 1122 cm$^{-1}$ indicates the acetal formation after crosslinking of PVA with aldehyde group of glyoxal [33]. After crosslinking with GLY peaks appears at 2567 $cm^{-1}$ become shifted.

In BA crosslinked TPVA, the intense peak at 665 cm−1 is attributed to vibration of B–O bond. In addition, the absorption band near 1407 $cm^{-1}$ is assigned to the anti symmetric stretching vibration of the B–O bond [48]. The band at 1093 $cm^{-1}$ was due to the stretching of B-O–C, which confirms the condensation reaction of PVA with boric acid. The existence of B–O–B linkage was proved by the peak located at 783 $cm^{-1}$, indicating the condensation of boric acid with itself.

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# Chapter 4

# CHARACTERIZATION OF THIOLATED POLYVINYL ALCOHOL (TPVA)

### 4.1. Introduction

The modification of conventional polymers has been of interesting technique in the preparation of new materials with improved properties. Among from huge community of polymer, PVA has gotten attention since the beginning of the nineteenth century in various industrial applications [1]. PVA was first prepared by Hermann and Haehnel in 1924 by hydrolyzation of poly(vinyl acetate). Due to the abundance of hydroxyl groups in the structure, PVA has often been used as the starting material for diverse reactions, such as esterification and etherification. Esterification of PVA with acid chloride anhydride, carboxylic acid and other acid has been widely used [2-13]. The extent of modification of the surface as well as bulk can be controlled by proper selection of experimental conditions like components and reaction conditions.

In addition to esterification of PVA, crosslinking is necessary to improve the structural integrity of the modified PVA in aqueous medium. Several crosslinkers that are well known for the crosslinking of PVA include phosphoryl chloride, epichlorohydrin, tri-sodium tri-metaphosphate and adehydes [14-19]. The thermal transition and viscoelastic behavior of the alginate/PVA blends were investigated by differential scanning calorimetry and dynamic mechanical analysis. The melting point of the PVA component was depressed systematically with increasing alginate content in the blends [20]. Park *et al***,** investigated the DSC results for the PVA gels. It displayed depressions of the melting and crystallization temperatures, as well as a decrease of the heat of fusion, when compared to non crosslinked PVA free of crosslinker [21].

Shude *et al* 2006, stated the preparation of four crosslinked PVA-TMC membranes with different degrees of crosslinking by applying trimesoyl chloride (TMC)/hexane to the surfaces of dried PVA membranes [22]. FTIR-ATR spectroscopy revealed that PVA-TMC membranes had asymmetric molecular structures. The degree of crosslinking was estimated by the loss of hydroxyl groups from FTIR-ATR spectra by using the peak integration method. DSC and TGA curves showed that crosslinked PVA-TMC membranes had higher thermal stabilities than the virgin PVA film. In addition, TGA/DTG thermograms of PVA-TMC membranes were investigated to understand the pyrolysis mechanism, which was a combination of elimination of water or trimesic acid followed by the breakage of the main chain. In continuation of studies Ahmad *et al*, stated the characterized studies, of GA/PVA/PVP-I blend films by FTIR spectroscopy, DSC and TGA [23].

Yoon *et al*, investigated the preparation of resistant Starch/PVA blend films plasticized by glycerol and crosslinked by glutaraldehyde and STMP. The crosslinking evidence of STMP with PVA/PVP was successfully confirmed by FTIR and mechanical studies [24]. Uslu *et al,* carried out the characterization of PVA/boron fiber produced by the electrospining method by SEM, DSC and FTIR studies [25]. Christie *et al*, reported the surface morphology and DSC studies of freeze-thawed PVA hydrogels. The overall structure and stability were examined in terms of water content, fractional PVA dissolution, degree of crystallinity, and crystal size distribution. An increase in the number of freezing and thawing cycles served to reinforce existing crystals within the structure [26]. Recently, the freeze-thawed transparent PVA hydrogels have been investigated by the same techniques [27]. Lewandowska *et al*, investigated the miscibility and thermal stability of PVA/CS mixtures by DSC and TGA studies [28].

Lue *et al*, investigated the water states in PVA-fumed silica nano-composites by DSC measurement by calculating bound and free (and freezable) water states for homogeneous, heterogeneous or microphase separated polymers [29]. Ali *et al*, observed the electron beam irradiation effect on PVA/$V_2O_5$ xerogel by DSC, FTIR and XRD studies [30]. Quantitative analysis of glyoxal crosslinked PVA was described in this report. A convenient FTIR method has been established to analyze the degree of crosslinking in PVA [31]. Miyazaki *et al,* stated the role of boric acid on melting behavior of the PVA film by the comparative studies of XRD and DSC [32].

Nurkeeva *et al*, studied the effect of pH on the complexation, miscibility and radiation-induced crosslinking in PAA/PVA blend system. In this investigation, author used FTIR, TGA, DSC and SEM techniques to observe this effect by changing the structural properties of blends [33]. Homopolymer films of gellan and PVA and their films were studied by DSC and FTIR [34]. Zhang *et al*, reported the negative biodegradation of PVA modified by various aldehydes. The modification was observed by FTIR due to the formation of covalent acetals [35]. Bacterial cellulose (BC) and PVA based crosslinked and noncrosslinked composites were optimized by FTIR, DSC and XRD. The resulting composites could be good candidates for replacing traditional non-biodegradable plastics [36].

Thermal degradation mechanism of PVA/silica nanocomposite has studied by coupled FTIR/TG analysis. Evaluation of gasses at different degradation steps have been successfully reported by this coupled technique [37]. Thermal degradation studies of polymethacrylates containing carboxylic groups were investigated by using TGA/FTIR techniques. In further observation, the nanocomposites segmented polyurethane and commercially available nanoclays were studied using TGA coupled with FTIR spectroscopy [38]. A comparative study of TG-FTIR and TG-MS spectra of pyrolysis of waste materials, biomass wood waste, waste tyre, refuse derived fuel (RDF) and waste plastic was performed by using coupled studies [39].

In our previous work, we have carried out the esterification and subsequent crosslinking. Various conditions, like reaction time, reaction temperature, reactants concentration and nature of crosslinkers were optimized. In this state-of-art, we have attempted to characterize the structural changes obtained by two step modification in PVA. The crosslinked TPVA films have been characterized by TGA, DSC, XRD, FTIR and coupled TG-FTIR techniques.

## 4.2. Experimental

### 4.2.1. Materials

PVA (Mw. 1,50,000 and the degree of hydrolysis 85%) was supplied from Sigma. TGA, sodium hydroxide, sulfuric acid, glyoxal (GLY) and methanol (HPLC grade) were purchased from Merck, India. Sodium trimetaphosphate (STMP) was supplied from Sigma and boric acid (BA) was supplied from S D Fine Chemicals. All were used without further preparation. Ultra-pure water, resistivity less than 18 MΩcm, produced by a Millipore Milli-Q system was used throughout the experimental work.

### 4.2.2. Esterification of PVA

Homogenous solution of 2 wt% PVA was prepared by dissolving 2 g PVA powder in 100 ml water under vigorous stirring for overnight at room temperature. Esterification reaction was carried out as previously (discussed in Chapter 2) optimized parameters i.e. 25% acid concentration for reaction time 24 h at reaction temperature 60 °C in presence of catalyst (1%) (v/v).

### 4.2.3. Crosslinking of Thiolated PVA

Above esterified PVA solution was used for further crosslinking reaction with different crosslinkers at optimized crosslinking conditions as per (in chapter 3). After completion of the reaction the mixture was slowly poured into 12 M sodium hydroxide solution at pH 12. A white precipitate was collected, washed repeatedly with water and methanol and dried under vacuum oven at room temperature.

### 4.2.4. Thiol Content Estimation

The amount of the involved and accessible thiol groups was successfully determined according to a protocol based on the *Volhard's silver nitrate method* [40]. The determination is based on the chemical affinity of silver by thiol groups. Following the protocol, 50 mg of dried TPVA has immersed in 50 ml of 0.01 M silver nitrate solution. The flasks were covered to avoid exposure to light and stirred in a shaker for 3 h prior to testing. The remaining silver nitrate was titrated with standardized 0.01 M potassium thiocyanate (KSCN) using iron ammonium sulfate hexahydrate as an indicator. The endpoint was detected when an excess of thiocyanate anion formed a red colored complex with the iron compound. The thiol content was expressed in mmol/g of polymer. In all cases, the tests were carried out in triplicate measurement.

### 4.2.5. Swelling Studies

The swelling studies of crosslinked thiolated PVA was assessed by the gravimetric method. Discussed in previous chapter 2 and 3. The swelling behaviour of the sample was specified by a function of the times and the weight was recorded as a gram of water uptake per minute. The swelling percent of the sample was calculated using the following equation [23]:

$$\text{Swelling (\%)} = \frac{W_s - W_d}{W_d} \times 100 \qquad eq.\ 1$$

Where, $W_s$ and $W_d$ are the weight of the samples in the swollen and dry states respectively.

### 4.2.6. Differential Scanning Calorimetry (DSC)

DSC studies of the samples were carried out on DSC-204 F1 Phoenix, Netzch, Germany system (Dept Chemistry, JMI Delhi). About 5-10 mg samples were loaded in the aluminum pan and the thermograms were run in the temperature range -20 to +300 ºC at a heating rate of 10 ºC/min. The heat of fusion ($\Delta H_f$) was obtained from the area under the melting thermogram. The crystallinity of the samples was obtained by the following expression:

$$\% \text{ Crystallinity} = \Delta H_f / \Delta H_f(\text{crys}) \times 100 \qquad \textit{eq. 2}$$

Where, $\Delta H_f$ is the heat of fusion of the sample and $\Delta H_f$(crys) is the heat of fusion of 100% crystalline PVA and was taken as 138 cal/g [41].

### 4.2.7. X-ray Diffraction (XRD)

X-ray diffraction on the crosslinked and noncrosslinked samples was recorded on PHILIPS, Holland, CuK$\alpha$ X-ray generator (Dept Textile Technology, IIT Delhi) to study the morphological changes in the material. Scanning was carried out in 2θ range of 5-60° at the wavelength of 1.54 A˚, filament current of 30 mA and voltage of 40 kV.

### 4.2.8. Thermogravimetric Analysis (TGA)

TGA studies were carried out using a Perkin–Elmer TGA-7 (Dept of Textile Technology, IIT Delhi) in the range of 50–600 °C. The heating rate was 10 °C/min. The measurements were made under a constant flow rate (20 ml/min) of nitrogen. The initial decomposition temperature (IDT) was obtained as the tangent at a point where the weight loss starts.

### 4.2.9. Thermogravimetric-Fourier Transform Infrared (TG-FTIR) Studies

TG-FTIR measurements of the crosslinked TPVA samples were performed on a NETZSCH TG 209 *F1 Iris*® simultaneously coupled to the BRUKER Optics FTIR *TENSOR*™ (Netzsh, Germany). The decomposition of gases at each degradation step were observed from TGA analyzer at temperature range 30-600°C (20 K/min) and measured by FTIR spectrometer in the scanning wave number range of 4000-600cm$^{-1}$.

## 4.3. Results and Discussion

The optimized crosslinking of esterified PVA was carried out with STMP at above optimized conditions. Characterization of the uncrosslinked and crosslinked thiolated PVA samples was carried out to investigate physical and chemical changes that are incorporated in the material by esterification. Distinct changes in the physical structure of PVA have been observed by different studies when the polymer was modified under inherent conditions. This leads to the enhancement of the thiol content in PVA with varying ratios of TGA and at the specific crosslinking reaction. The other factor guiding the investigation has been the variation of thiol content with different crosslinker at same conditions. The effect of crosslinker on various physical and chemical properties of crosslinked TPVA has been discussed in this section.

### 4.3.1. Influence of Acid Concentration

To investigate the influence of a combination of esterification and crosslinking on thiol content and swelling is presented in Figure 4.1. As we discussed in chapter 2 the esterification is strongly dependent on the TGA concentration therefore, higher concentration favored the ester formation. In our studies, the acid concentration variation observed from 5 to 25% with respect to PVA concentration and from the above stated studies (in chapter 3) the STMP is suitable crosslinker for our purpose.

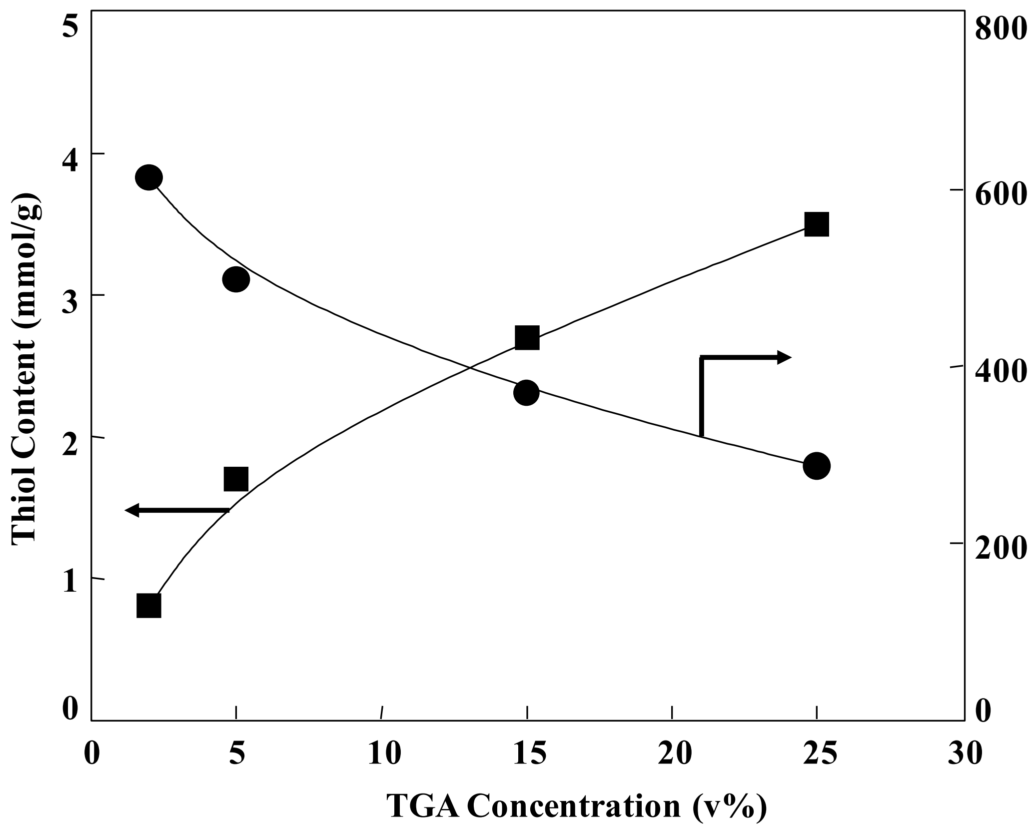

**Figure 4.1. Variation of the thiol content and swelling with TGA concentration. Reaction conditions: PVA; 2%, reaction time; 24 h, temperature; 60 °C, crosslinker; STMP, crosslinker content; 0.1%**

**Table 4.1. Variation of the thiol content and swelling with TGA concentration. Reaction conditions: PVA; 2%, reaction time; 24 h, temperature; 60 °C, crosslinker; STMP, crosslinker content; 0.1%**

| TGA conc. (%) | Thiol Content (mmol/g) | Swelling (%) |
|---|---|---|
| 2 | 0.8 | 613 |
| 5 | 1.7 | 498 |
| 15 | 2.7 | 369 |
| 25 | 3.5 | 287 |

The results suggest that the combination of crosslinking and esterification had more influence on the hydrophilicity than had individual modifications. The reaction conditions were adjusted so that the resulting thiol remains in the range of 0.5 to 4 mmol/g, so that we can monitor the influence of the esterification and crosslinking conditions on the physical structure of the PVA tabulated in Table 4.1.

#### 4.3.1.1. XRD Studies

X-ray diffraction pattern of pure PVA and STMP crosslinked TPVA samples having different thiol content are shown in Figure 4.2 and 4.3. The thiol content for these samples is between 0.5 to 3.5 mmol/g.

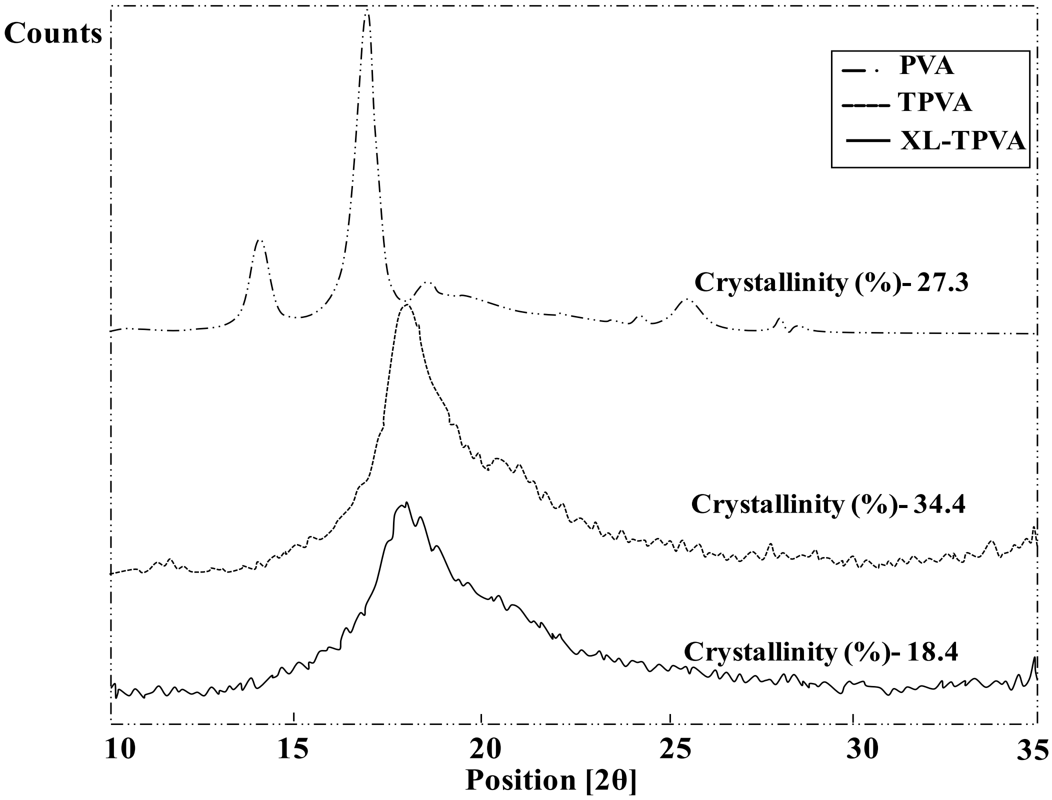

**Figure 4.2. X-ray Diffractogram of pure PVA, thiolated (TPVA) and STMP crosslinked TPVA**

The appearance of sharp reflections is evident from the XRD of pure PVA, is characteristic of crystalline and amorphous phases of conventional semi-crystalline polymers. Moreover, the pattern observed for pure PVA, shows several distinct crystalline peaks at $2\theta$ = 14.06, 16.93, 25.56 and 28.29°. In the XRD of the TPVA and crosslinked TPVA films the intensity of the peak at 19.3° become broader due to the involvement of two different modification steps. The peak at 19.3° is caused due to the crystallinity of the PVA. We can see that the addition of STMP greatly decreased the crystal peak around 19.3°. Moreover, the peak's height at the same angle decreased as STMP involved in the matrix. The esterification and crosslinking effect will reduce the crystallinity of the PVA.

The XRD scans for the modified PVA there were two peaks at 2θ = 14 and 16º which revealed a PVA crystal structure. With increasing TGA concentration at same crosslinker content however, the first peak disappears and second gradually shifted toward 2θ = 19°, indicated the distraction of a crystalline nature after simultaneous modification. The crystalline reflections for STMP crosslinked TPVA were found to occur at distinct angles. However, the crystallinity could be visualised to diminish as a result of crosslinking process. Other authors have also observed the amorphous nature of STMP induced crosslinking process [42]

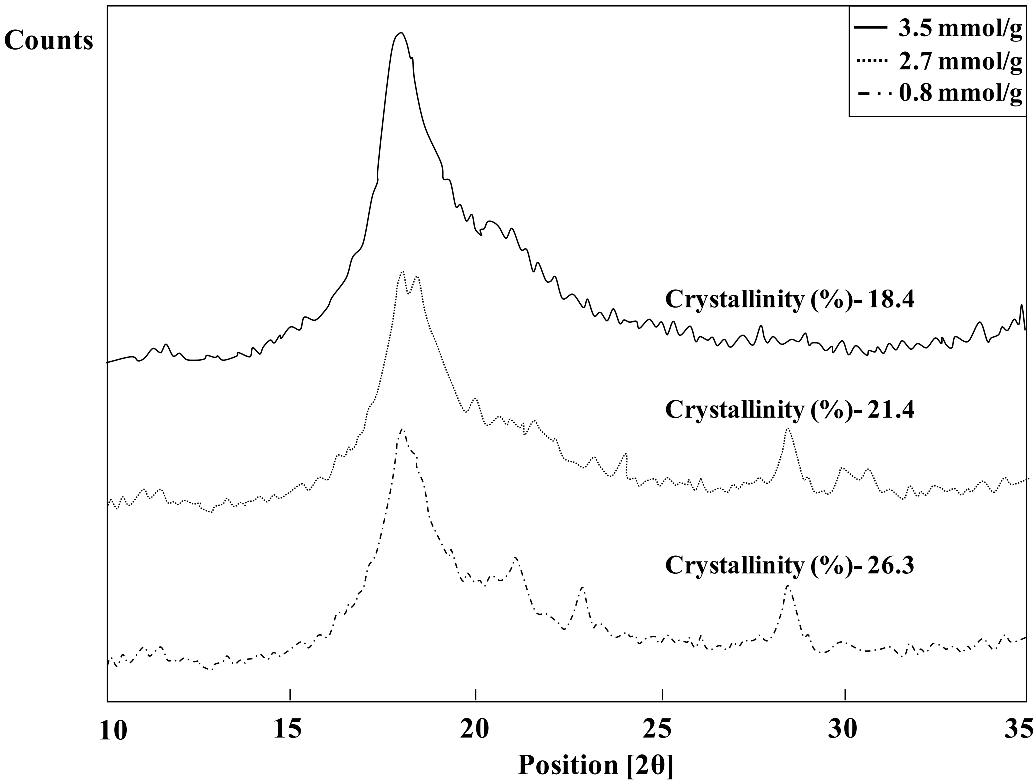

**Figure 4.3. X-Ray Diffractogram of STMP crosslinked TPVA samples with different thiol content**

#### 4.3.1.2. TGA Studies

The TGA results for pure PVA, esterified and crosslinked PVA films are shown in the Figure 4.4 and 4.5. Pure PVA showed a two-step decomposition pattern. The first step started at the beginning of the thermogram and continues upto 160 °C and the second one began around 240 °C. The first step of weight loss could be attributed to the loss of water, accompanied by the formation of volatile disintegrated products. The second step was mainly caused by the decomposition of the molecular chain, and the products were composed of small molecule carbon and hydrocarbon. TGA thermogram shows that the thermal stability of pure PVA is increased after modification by two consecutive steps esterification and crosslinking shown in Table 4.2.

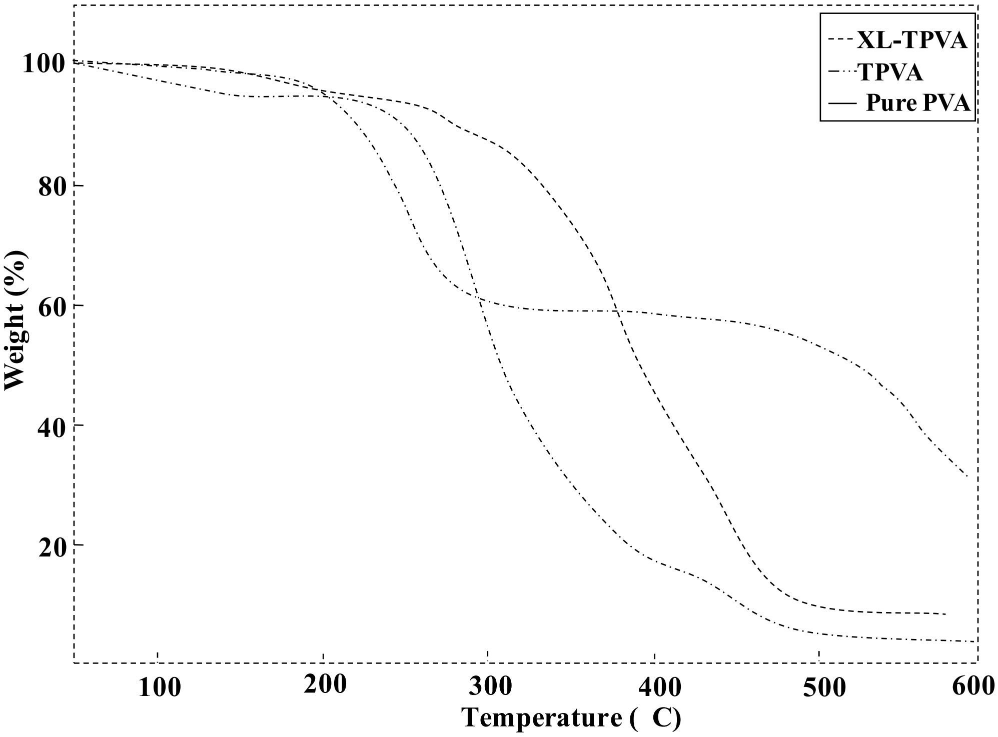

**Figure 4.4. TGA thermogram of pure PVA, TPVA and STMP crosslinked TPVA with different thiol content**

The thermal stability of PVA film is increased after modification. Initial weight loss in the samples (50 to 200 °C range) is lower than pure PVA and could be explained by evaporation of residual water content of the hydrophilic components. The second weight loss occurs at 170–200 °C. Thiolated PVA shows further degradation arising at 180 °C as compared to 220 °C for pure PVA. This shows thermally unstable nature of the thiolated polymer. Crosslinking certainly increased the thermal stability and IDT moves to 340 °C.

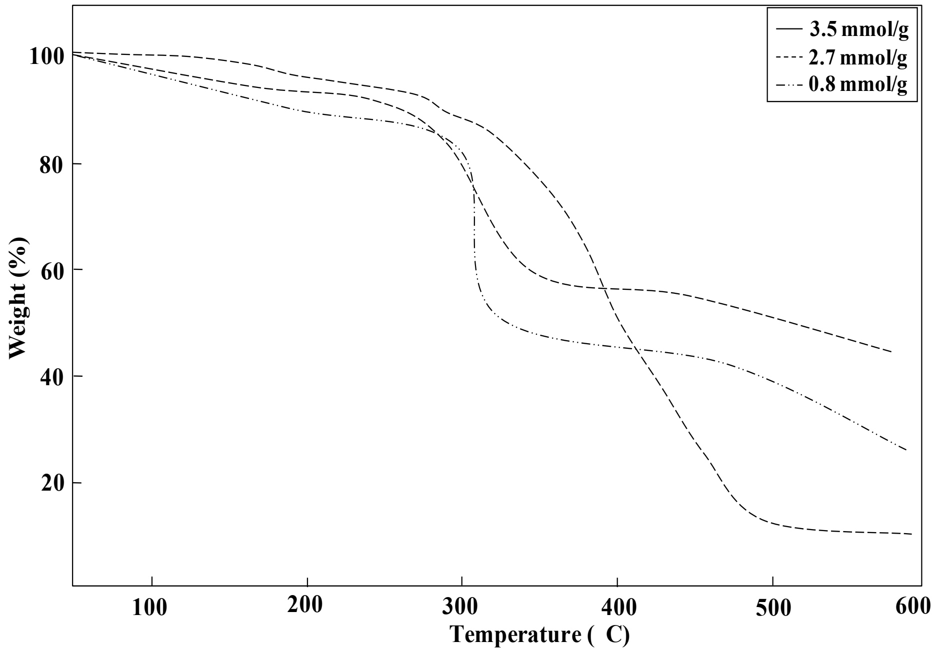

**Figure 4.5. TGA thermogram of STMP crosslinked TPVA samples with different thiol content**

**Table 4.2. Description of TGA thermograms of pure PVA, STMP crosslinked TPVA samples with different thiol content**

| **Sample** | **Thiol Content (mmol/g)** | **IDT (°C)** | **$T_{50}$ (°C)** |
|---|---|---|---|
| Pure PVA | - | 225 | 345 |
| TPVA | 3.9 | 202 | 362 |
| STMP-TPVA (A) | 0.8 | 260 | 443 |
| STMP-TPVA (B) | 2.7 | 280 | 470 |
| STMP-TPVA (C) | 3.5 | 340 | 485 |

### 4.3.1.3. DSC Studies

DSC thermograms of the pure PVA, TPVA and STMP crosslinked TPVA samples with thiol content (3.5 mmol/g) are presented in Figure 4.6 and 4.7. The $T_g$ of the pure

PVA is around 70 °C, which is similar to the reported in other works [43,44]. After thiolation of PVA, the $T_g$ decreases due to the formation of strong covalent bond while after crosslinking the $T_g$ value increases due to the diminishing degree of crystallinity. These effects suggest a serious restraint of the amorphous relaxation of PVA main chains, arising from the intimate incorporation with the crosslinker component. Description of above stated DSC studies is tabulated in Table 4.3.

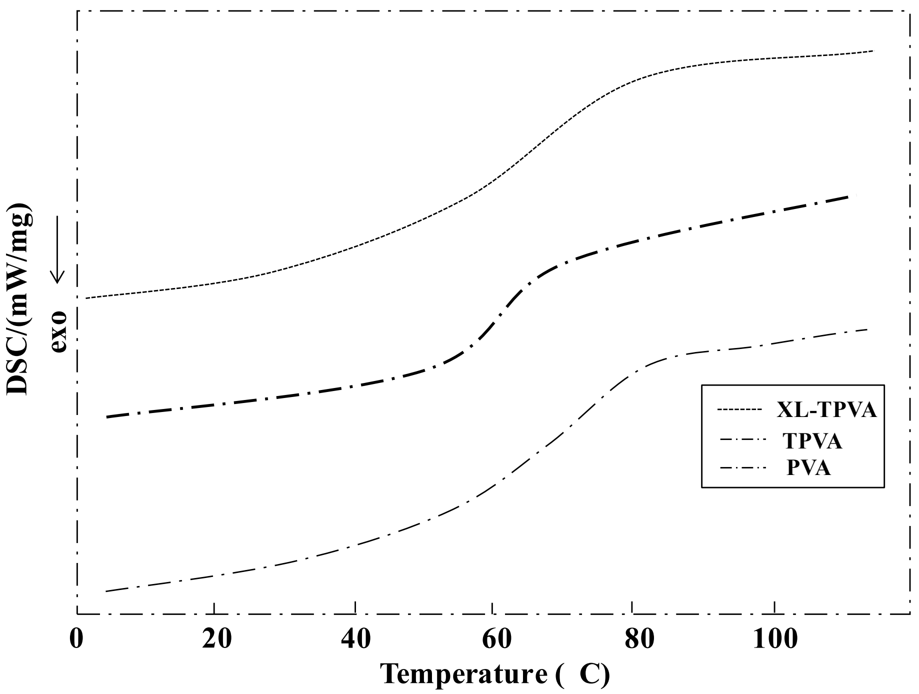

**Figure 4.6. DSC thermogram on glass transition region of Pure PVA, Un cross-linked & cross-linked TPVA at different thiol content**

**Table 4.3. Description of DSC thermograms of pure PVA, STMP crosslinked TPVA samples A (0.8 mmol/g), B (2.7 mmol/g) and C (3.5 mmol/g)**

| **Sample** | **$T_g$ (°C)** | **$T_m$ (°C)** | **ΔH (J/g)** | **Crystallinity (%)** |
|---|---|---|---|---|
| Pure PVA | 83 | 191 | 39.7 | 29.2 |
| TPVA | 70 | 205 | 45.7 | 31.2 |
| STMP-TPVA (A) | 65 | 170 | 30.2 | 24.7 |
| STMP-TPVA (B) | 70 | 174 | 27.9 | 20.2 |
| STMP-TPVA (C) | 76 | 177 | 22.9 | 16.6 |

Pure PVA shows sharp endothermic peak at 190 °C. However, after esterification TPVA films indicate a new broad peak at the lower temperature zone (150-180 °C), which is probably assigned the melting of the quasi-crystalline phase. The quasi-crystalline phase can be regarded as defects in the pure PVA crystalline phase. TPVA shows melting at high temperature at 205 °C. On the other hand, after crosslinking of TPVA with STMP the quasi-crystalline phase is disappears due to the involvement of free hydroxyl groups which remain after esterification in the crosslinking process.

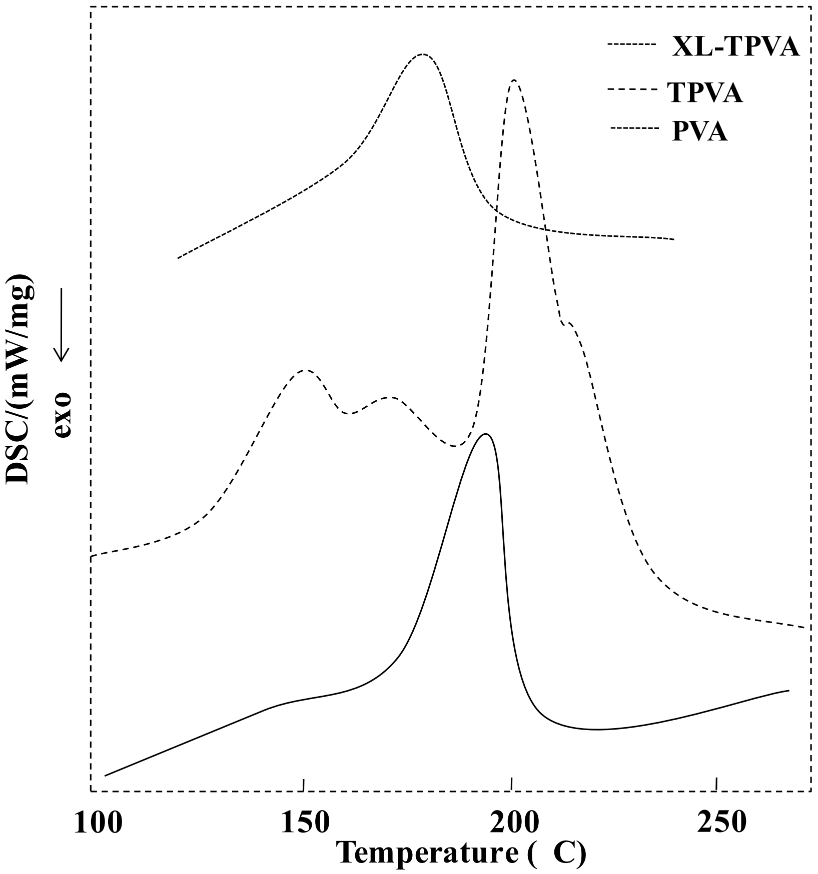

**Figure 4.7. DSC thermogram on melting temperature region of Pure PVA, Un cross-linked & cross-linked TPVA at different thiol content**

The further DSC studies of STMP crosslinked samples are shown a rapid increase in the glass transition temperature ($T_g$) and decrease in the enthalpy of fusion ($\Delta H$) and melting temperature ($T_m$). The DSC thermograms of STMP crosslinked TPVA samples with different thiol content are presented in Figure 4.8 and 4.9.

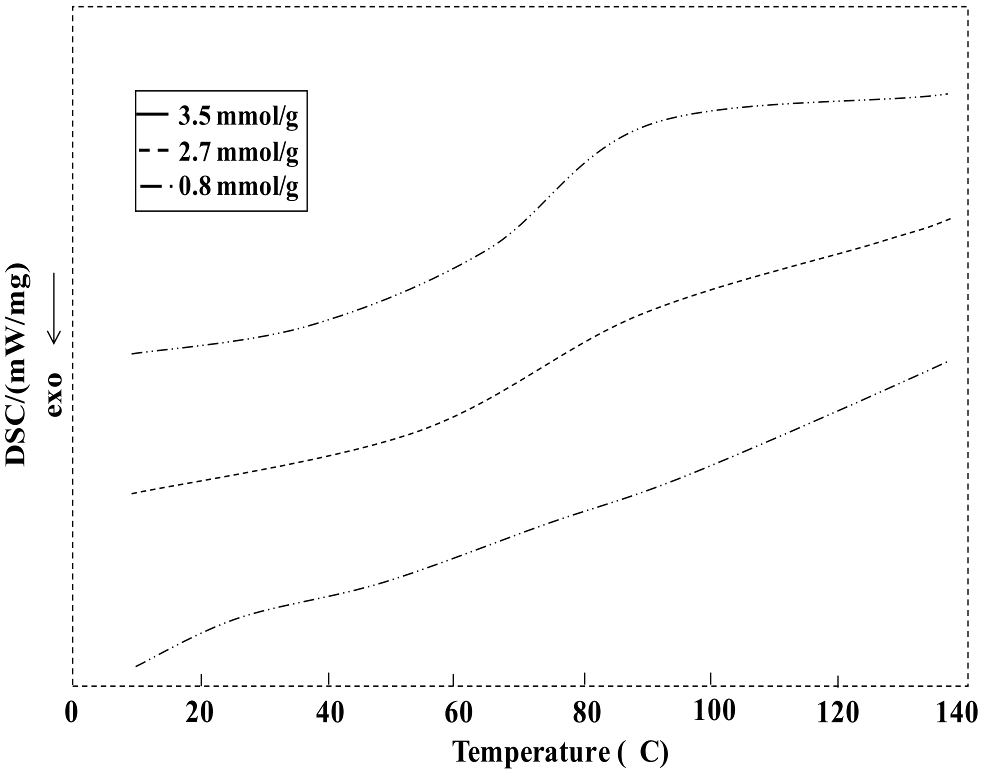

**Figure 4.8. DSC thermogram on glass transition region of STMP crosslinked TPVA with different thiol content**

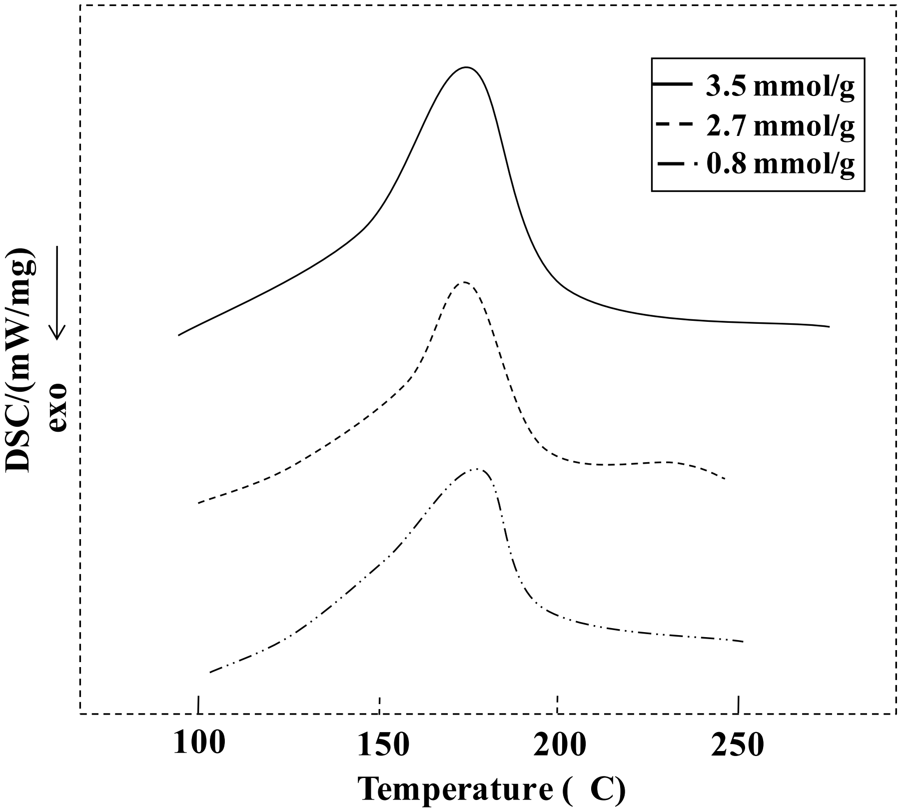

**Figure 4.9. DSC thermogram on melting temperature region of STMP cross-linked TPVA at different thiol content**

### 4.3.2. Influence of the Nature of the Crosslinker

The effect of this variation has been taken into consideration and studied through different techniques as given below. The samples taken for analysis are tabulated in Table 4.4.

**Table 4.4. Variation of the thiol content of crosslinked TPVA samples with different crosslinker. Reaction conditions: crosslinker content, 0.1%; crosslinking time, 30 min; temperature, 60 °C.**

| Crosslinker | Thiol Content (mmol/g) |
|---|---|
| STMP | 3.5 |
| BA | 3.1 |
| GLY | 2.9 |

#### 4.3.2 .1. XRD Studies

The X-ray diffraction patterns of crosslinked TPVA samples with different crosslinker are presented in Figure 4.10. The thiol content of these samples are lies in between 2.5 - 3.5 mmol/g.

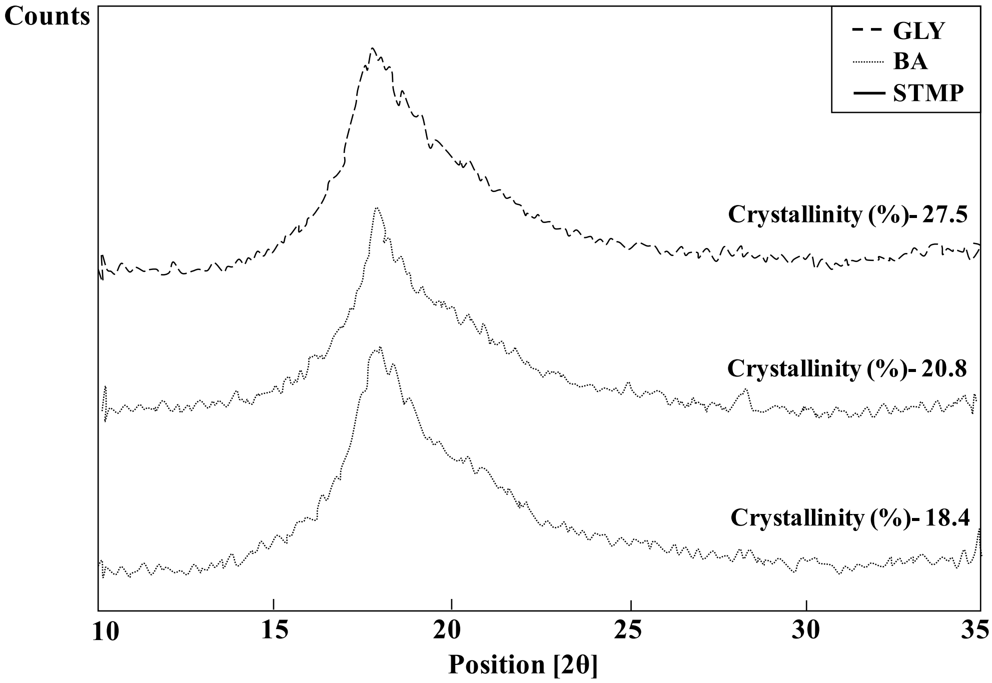

**Figure 4.10. X-ray diffractograms of crosslinked samples with different crosslinker**

The action of three crosslinker is similar the magnitude of their impact is different. The crystallinity of all the crosslinked samples showed lower both GLY and BA crosslinked samples as compared to the STMP crosslinked one. It seems that the GLY and BA leads to more efficient interlinking of chains and hence the crystallization process is hindered to some extent.

### 4.3.2.2. DSC Studies

DSC thermograms of $T_g$ and $T_m$ separately for the crosslinked TPVA samples with different crosslinkers are presented in Figure 4.11 and 4.12 also tabulated in Table 4.5. In order to explain these results, one has to take into account that the studied system is a very complex one. It is known that PVA is a semicrystalline polymer in which high physical interactions between the polymer chains, due to hydrogen bonding between the hydroxyl groups [45].

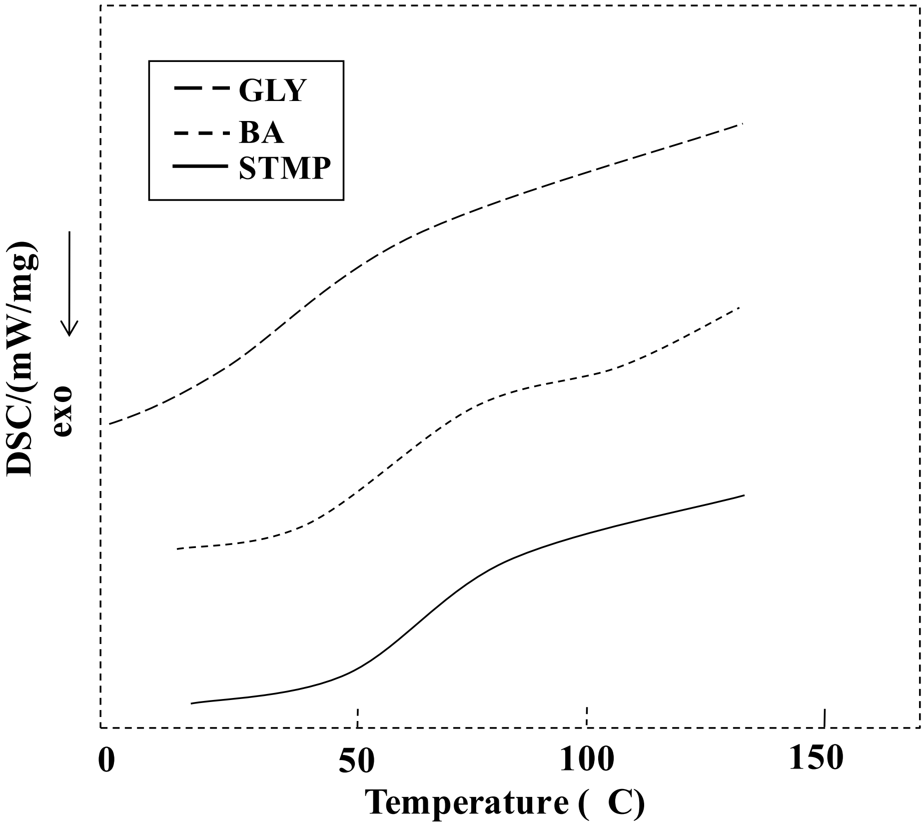

**Figure 4.11. DSC thermogram on glass transition region of TPVA crosslinked samples with different crosslinkers**

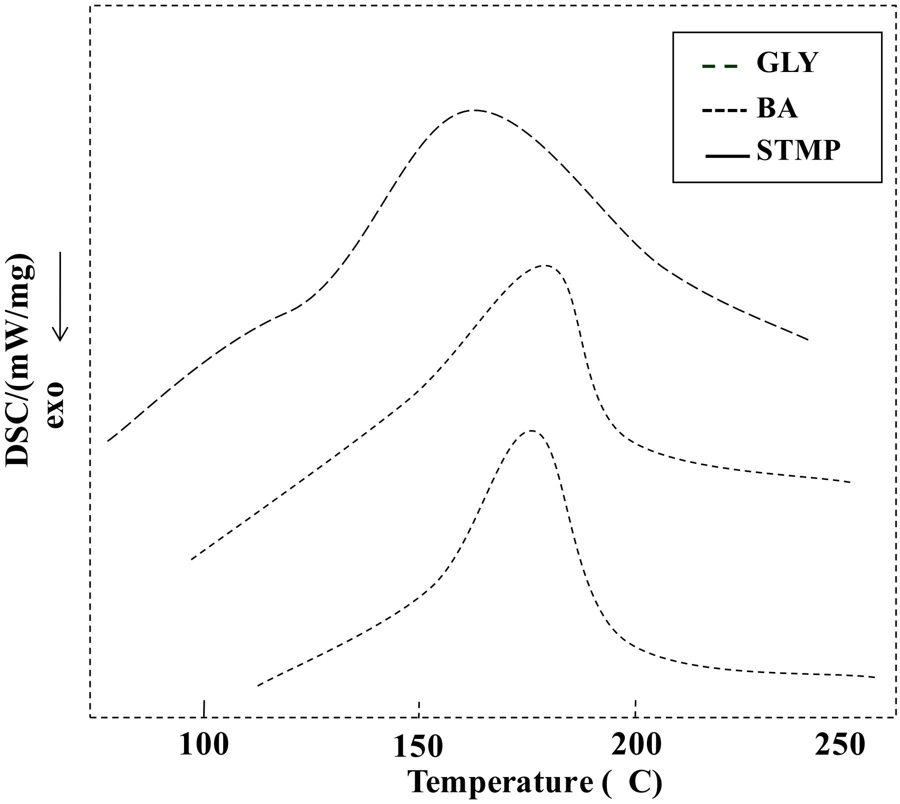

**Figure 4.12. DSC thermogram in the melting region of crosslinked TPVA samples with different crosslinker**

**Table 4.5. Description of DSC studies of crosslinked TPVA samples with different crosslinker**

| **Sample** | **Tg (°C)** | **Tm (°C)** | **ΔH (J/g)** | **Crystallinity (%)** |
|---|---|---|---|---|
| STMP | 65 | 175 | 22.8 | 16.6 |
| BA | 61 | 177 | 24.8 | 17.8 |
| GLY | 45 | 165 | 37.2 | 26.9 |

The introduction of a different crosslinking agent affects both, crystallinity and physical network, originating variations in the $T_g$ values of the system. The crosslinking increases the rigidity and the new moieties introduced can affect $T_g$ in a different way, depending on their bonding strategies. In our case all three crosslinker STMP, BA, GLY created the bridges between the polymer chains which are not rigid ones, but flexible sequences of phosphate, borate and acetal formation, respectively.

Parallel DSC studies show a rapid decrease in the enthalpy of fusion ΔH and melting temperature $T_m$ and testify to the diminution of crystallinity with crosslinking [45]. This may be due to the crosslinking of PVA chains which restricts the arrangement of chains due to the crystal structure. It has been reported by several authors that the crystallinity of crosslinked samples decreases with crosslinking [32,46]. In crosslinking with GLY, the endothermic peak of TPVA decreased along with the depression of the melting temperature. However, the crystalline region is higher than the other two crosslinkers.

### 4.3.2.3. TG-FTIR Studies

The coupled TG-FTIR study is used and the on-line analysis of the evolved gases from material and the performed. Figure 4.13 depicts the relative mass change of the pure PVA sample and the Gram-Schmidt trace as the overall IR intensities. Gram-Schmidt plots are useful as they provide information related to the total IR absorbance of the evolved components over the entire spectral range [47].

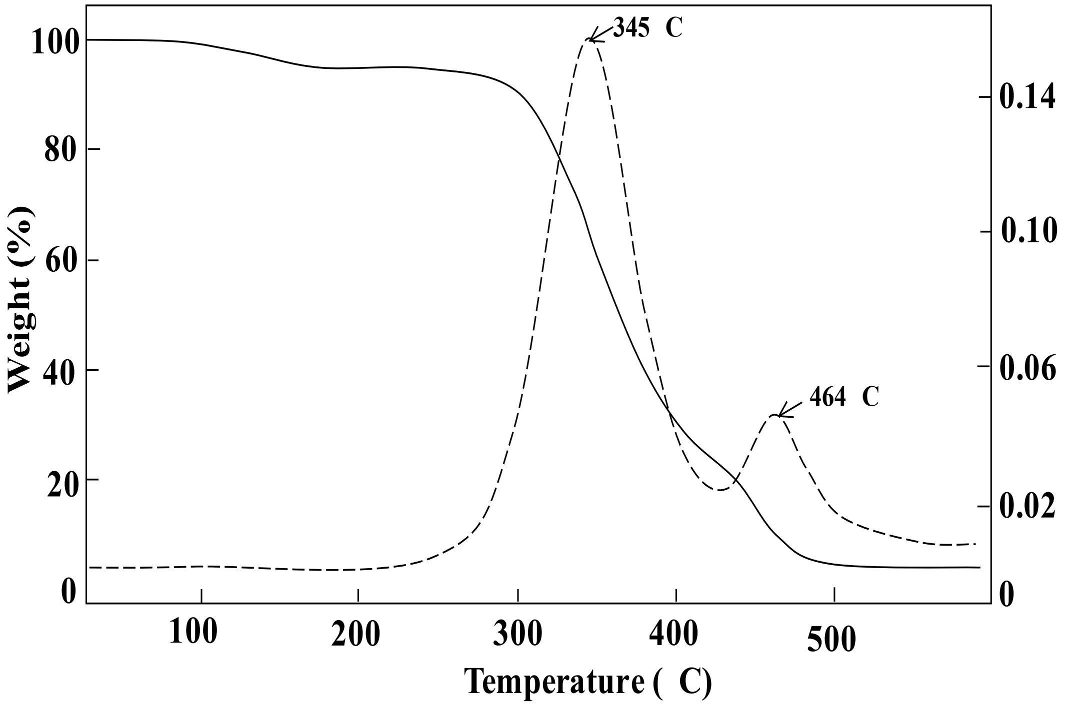

**Figure 4.13: TG thermogram of pure PVA ( )—and Gram-Schmidt trace ( ) - -**

There are three distinct and well-separated region (80-140 °C, 300-450 °C and 450-550 °C) in the thermogravimetric (TG) curve have been shown. Therefore, the thermal degradation of PVA can be roughly regarded as a three-step-degradation. To avoid the overlap of evolved gases from different degradation steps, the samples were heated at three temperature points, 145 °C, 345 °C and 476 °C with reference spectra from the NIST database. The spectra are shifted in the absorbance axis. Figure 4.14 shown the comparative spectra with reference water at temperature 145 °C indicates the elimination of residual water from the matrix indicating the dehydration process.

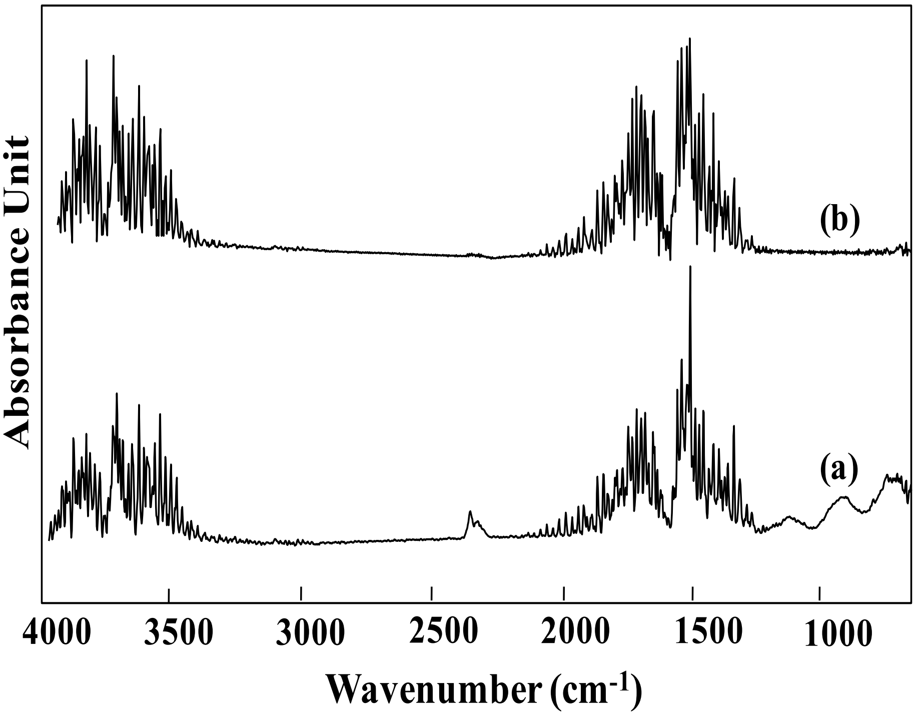

**Figure 4.14. FTIR-spectrum at 145 °C pure PVA (a) with the reference spectrum of water (b)**

The samples were then heated around the peak degradation temperature (Tp) of the first degradation step 345 °C that is obtained from TGA analysis till the degradation was completed. FTIR spectra of pure PVA at 345 °C showed in Figure 4.15. However, as the present study employs a low hydrolyzed (85-88.7%) PVA and a big amount of acetate groups remain in PVA molecular chains. As the acetate groups are randomly inserted between hydroxyl groups in PVA chain therefore, the elimination of $H_2O$ and residual acetate groups occurs simultaneously. In addition to water, a big amount of acetic acid is also observed during the first degradation step. The narrow and acute peak at 3550 cm$^{-1}$ and 1760 cm$^{-1}$ belong to the stretching vibration peaks of OH and COO$^-$ of gaseous acetic acids, respectively [48].

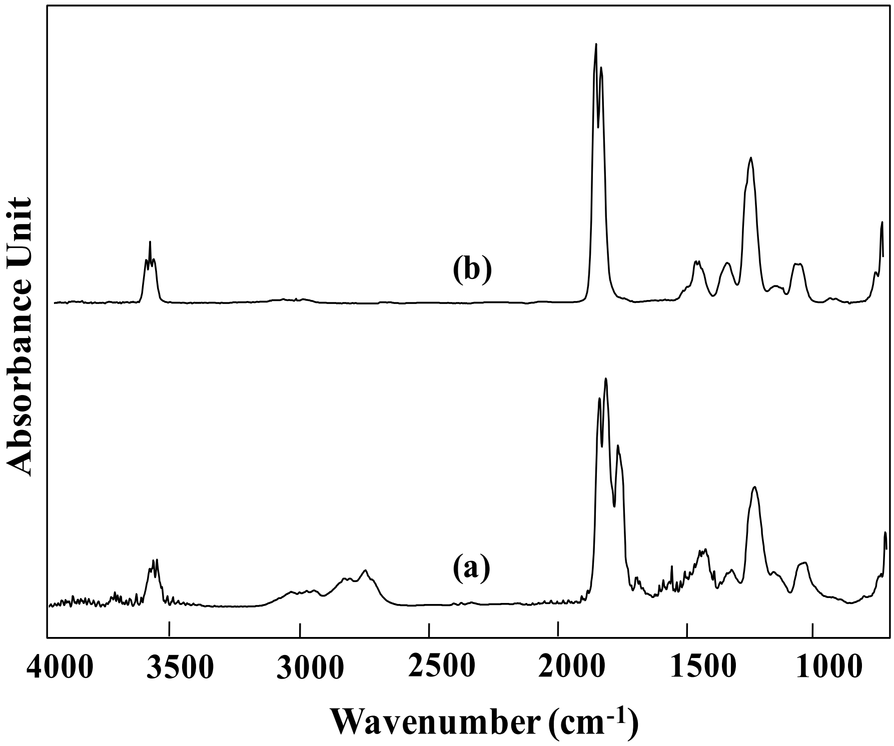

**Figure 4.15. FTIR spectrum at 345°C of pure PVA (a) with reference spectra of acetic acid (b)**

Finally, the samples were heated around Tp of the second degradation step till the degradation was finished. The comparative FTIR spectra of pure PVA at 464 °C were shown in Figure 4.16. The pure PVA display absorbance peaks in the region of 2395–2268 cm$^{-1}$. This is representative of $CO_2$ due to its indicative asymmetric stretching of the carbonyl group [49]. Carbon monoxide which is represented by the functional group CO at the absorption band between 2240 and 2060 cm$^{-1}$ was present. The CO functional group is representative of carbon monoxide as detailed by several authors [50-52]. It was anticipated that the FTIR spectra have observed increased levels of CO with the high temperature pyrolysis of PVA.

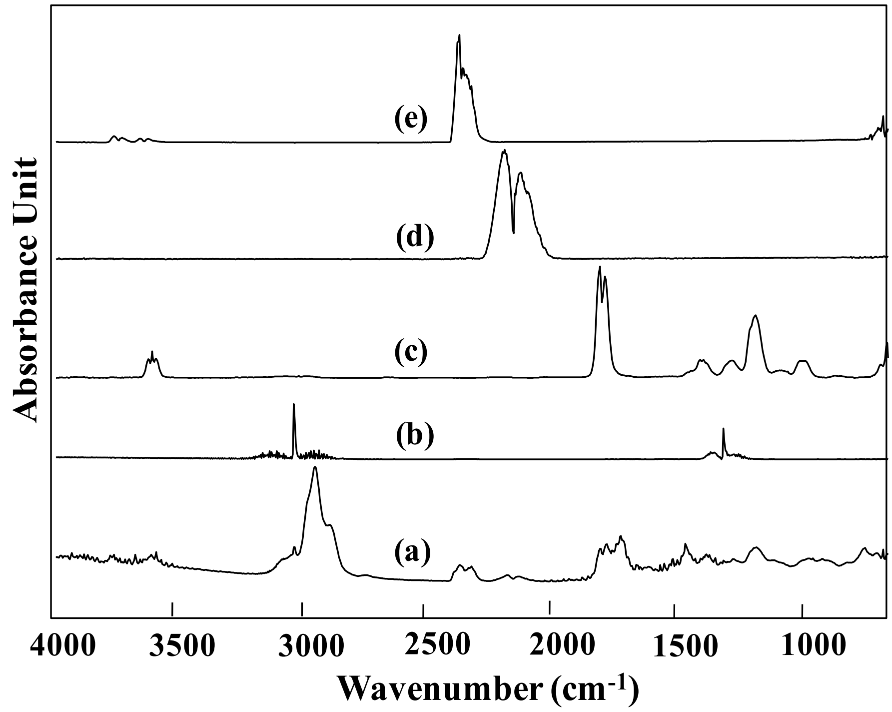

**Figure 4.16. FTIR spectrum at 464°C pure PVA (a) and reference spectra of methane (b), acetic acid (c), carbon monoxide (d) and carbon dioxide (e)**

TG and Gram-schimd curve of crosslinked TPVA sample with different crosslinker having varying thiol content is presented in Figure 4.17.

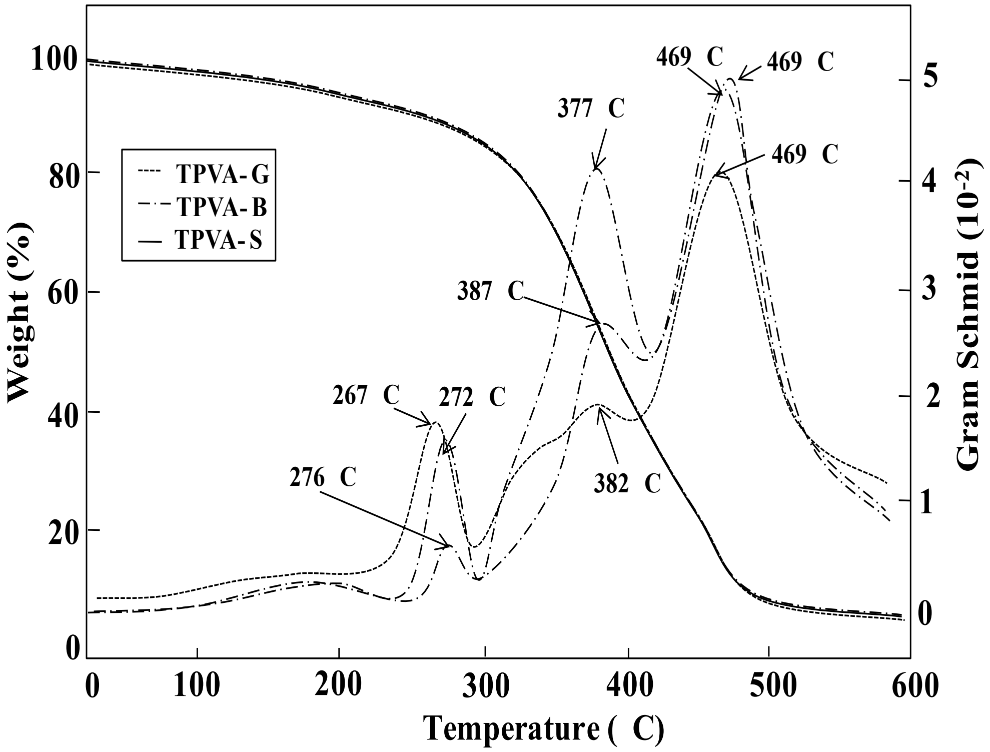

**Figure 4.17. TG thermograms and Gram-Schmid traces of crosslinked TPVA samples**

The thermograms of three samples TPVA-S, TPVA-B and TPVA-G have nearly the same decomposition behavior.

To compare the evolved gases of the above three samples, the FTIR spectra in the region below 200 °C, about 275 °C, 385 °C and 470 °C are shown separately in the next four figures with the most relevant reference substances from the NIST database. The spectra are shifted in the absorbance axis. In Figure 4.18 shows the FTIR spectra of crosslinked TPVA samples with different crosslinker at below 200 °C all samples evolved the water. The intense peak appears at absorbance 3300 $cm^{-1}$ is ice on the MCT detector.

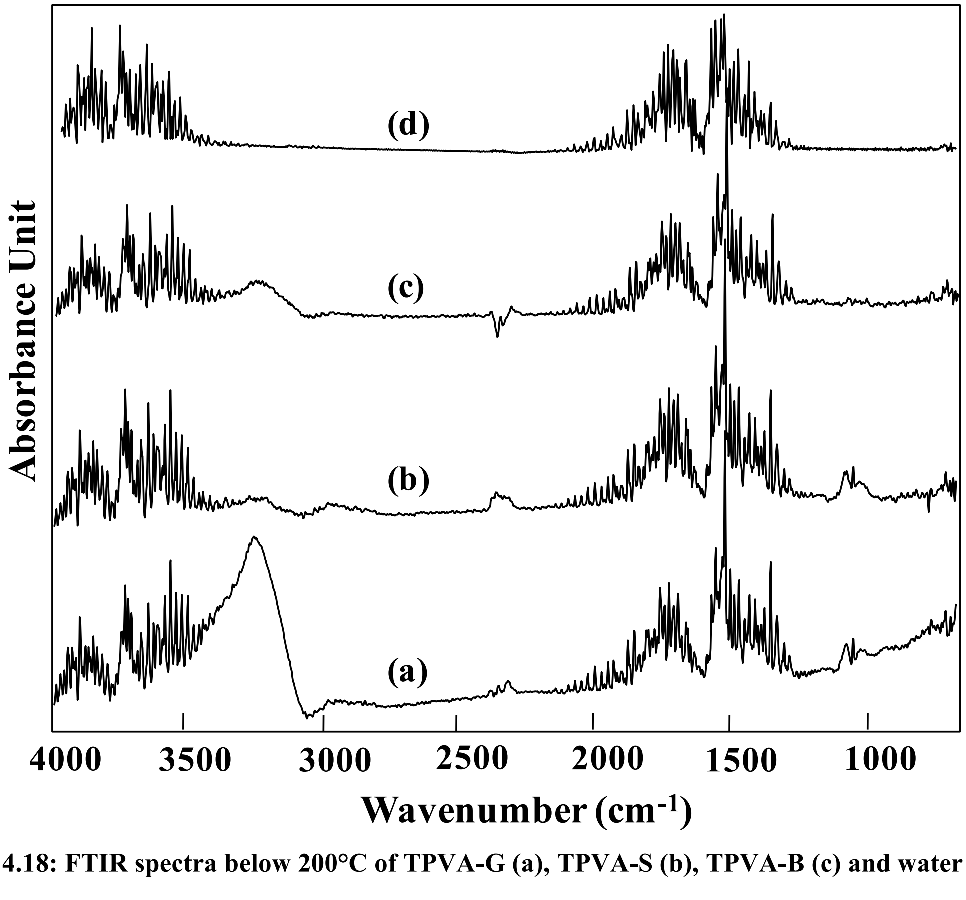

**Figure 4.18: FTIR spectra below 200°C of TPVA-G (a), TPVA-S (b), TPVA-B (c) and water (d)**

The FTIR spectra of different crosslinked TPVA samples at 275 °C shown in Figure 4.19. The most important representation of this spectrogram is to show the evolution of sulfur containing gaseous being prominent for this material. The $CS_2$ evolution is investigated at 1575–1500 cm$^{-1}$ and the liberation of COS is observed at 2150–2050 cm$^{-1}$ [53-55]. With respect to the TGA-FTIR spectra the present study was not able to detect $H_2S$, $SO_2$ and any other relevant sulfur containing gas.

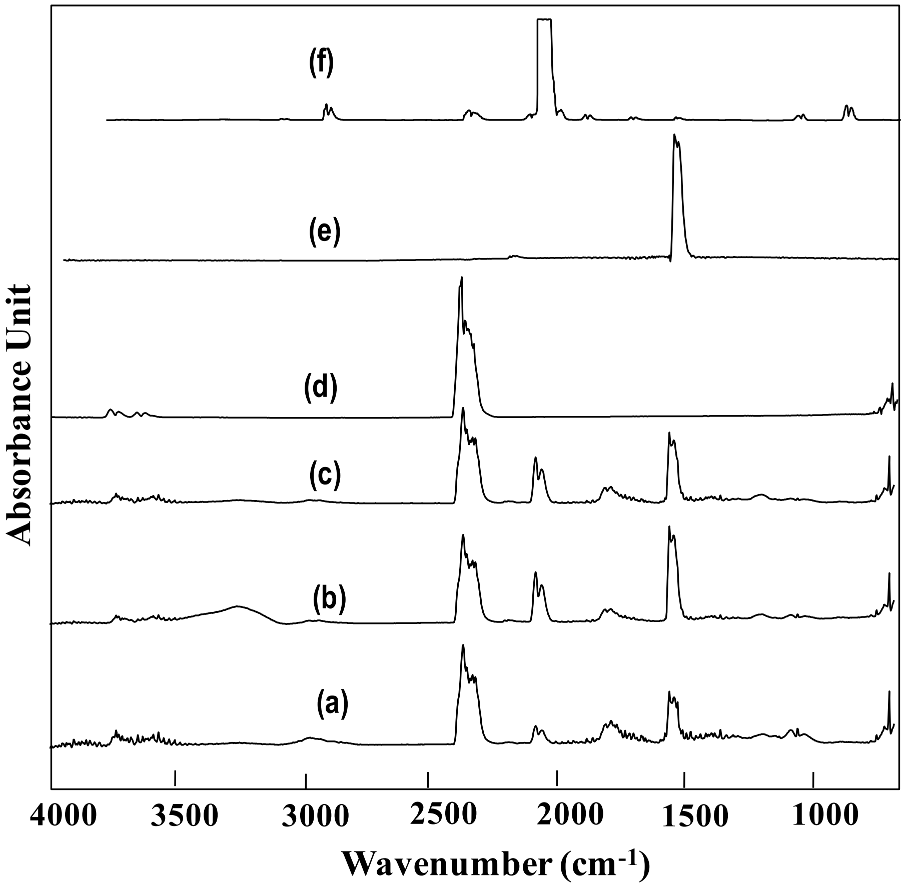

**Figure 4.19. FTIR spectra at about 275°C of TPVA-G (a), TPVA-S (b), TPVAB (c), carbon dioxide (d) carbon disulfide (e) and COS (f)**

The FTIR spectrogram of different crosslinked samples at 385 °C are shown in Figure 4.20. Spectra investigate the increase intensity of acetic acid, $CO_2$ and CO as compared with pure PVA due to the involvement of more respective components in the system. The band appears in the range of 2240-2060 cm$^{-1}$ due to the liberation of $CO_2$ gas at the decomposition of material at this temperature. Figure 4.21 represents the FTIR spectra of above same samples at very high temperature 470 °C. At this temperature the respective material is completely decomposed. At the spectral range of 3100–2900 cm$^{-1}$, it appears due to the evaluation of methane.

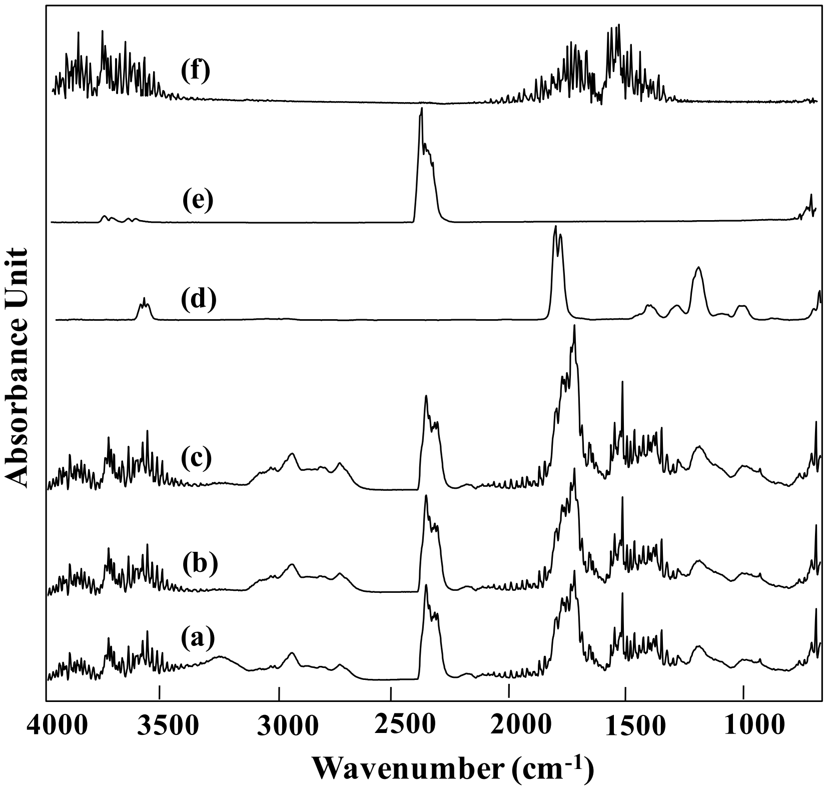

Figure 4.20. FTIR spectra at about 385 °C of DG (a), DS (b), DB (c), acetic acid (d), carbon dioxide (e) and water (f)

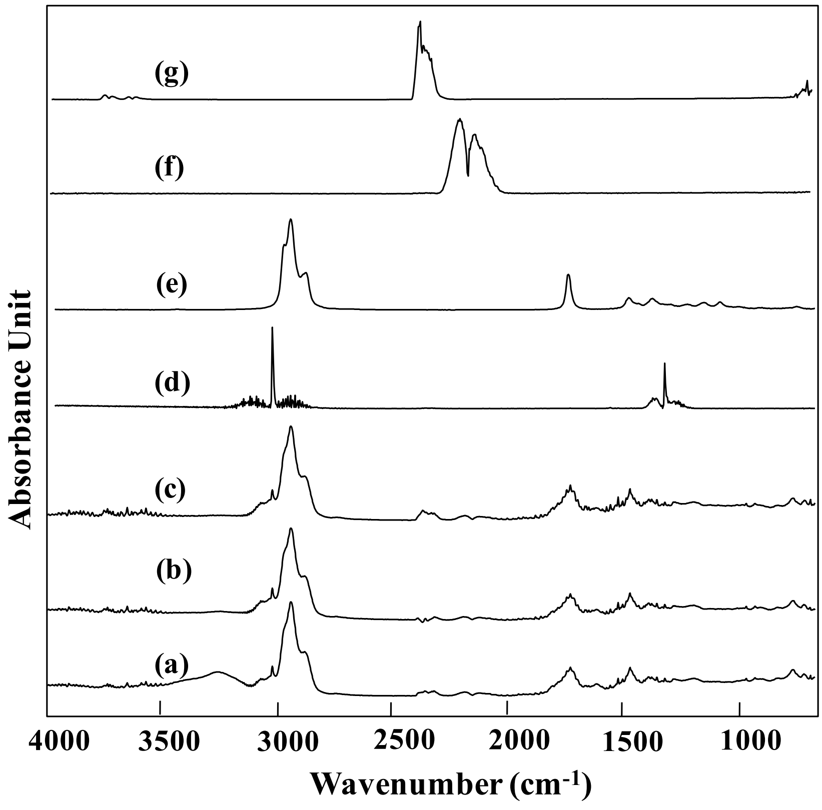

Figure 4.21. FTIR spectra at about 470 °C of TPVA-G (a), TPVA-S (b), TPVA-B (c), methane (d), 7-Tridecanone (e), carbon monoxide (f) and carbon dioxide (g).

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# Chapter 5

# ARSENIC REMOVAL FROM WATER BY CROSSLINKED TPVA AS CHELATING MATERIAL

## 5.1. Introduction

In the process of human evolution, some of the issues confronting today's society are safeguarding the natural environment and maintaining a good quality of life. However, a slight imbalance in any equilibrium in the environment is bound to manifest itself in the form of what can be called an environmental hazard. Arsenic (As) poisoning has come to be known as the worldwide problem of high priority. Several reports estimated that 130 million people across the world have been exposed to levels of arsenic in their drinking water that exceeds the WHO recommended limit of 10 ppb [1,2]. At present, among 21 countries in different parts of the world, the USA, Afghanistan, Bangladesh, Cambodia, Canada, Hungary, China, Chile, Argentina, India, Japan, New Zealand, Mexico, Mongolia, Myanmar, Nepal, Pakistan, Poland, Taiwan, Thailand, Vietnam and Siberia have reported high levels of arsenic concentration in their groundwater [3-6].

Arsenic has been a centre of controversy till fourth century BC. It is found in a wide variety of chemical forms in the environment [7]. Arsenic can harm the central and peripheral nervous systems as well as heart and blood vessels and can cause serious skin problems. It also causes birth defects and problems in the reproductive system. In a developing country, attribution of medical expenditure to arsenic-related diseases imposed an extra burden on the already overburdened public provision of medical care [8]. Arsenic can exist in a variety of oxidation states (-3, 0, +3 and +5) in inorganic and organic forms in many environmental matrices such as natural water and soils [9]. Unlike organic pollutants, arsenic cannot be transformed into non-toxic materials. It can only be transformed into a form that is less toxic to organisms in the environment. Because arsenic is a permanent part of the environment, there is a long-term need for regular monitoring at sites where it occurs naturally and anthropogenically at elevated concentrations. At present, the most important challenge for the engineers, scientists and policy makers is to find an immediate and safe alternative for areas where the drinking water supply contains arsenic.

Precise knowledge of the arsenic compounds present in a system is required for an accurate assessment of the environmental impact of arsenic, which has resulted in an increasing need of analytical method for their determination at micro or even ultra trace levels. In the last decades, a large amount of scientific and technological work has been devoted to develop new technologies for arsenic remediation that seek to minimize costs of investment, operation and maintenance [10]. Various treatment technologies have been developed for arsenic removal from drinking water (discussed in chapter 1). The commonly used technologies are classified as physical methods, i.e., ion-exchange, adsorption, electrochemical techniques and membrane process; chemical processes, i.e., coagulation, sedimentation, filtration, precipitation; photochemical technologies and biological methods i.e., bacterial removals and phytoremediation [11-20]. Several of them are effective for arsenate As(V), removal but not much for arsenite As(III) due to its complex aqueous chemistry. These issues have highlighted the urgent needs for the development of an environmental-friendly and enduring technology for arsenic removal without any need of additional pre-treatment process.

For the selective binding of arsenic from the water, polymeric materials have been investigated and patented successfully [21]. The chelating polymers designed either by the polymerization of monomers possessing the desired sites (i.e. nitrogen, oxygen or sulphur) or by reaction with low molecular weight compounds containing different functional groups (i.e. $–NH_2$, $–SO_3H$, $–NH_4OH$, –SH and many others). The available free coordination sites of chelating polymers usually binds with metal ions through coordinate or coordinate-covalent bonds.

Hydrogels are 3-D networks of hydrophilic polymers imbibing large amount of water. Due to their ability to change shape and volume in response to external stimuli, hydrogels have been studied extensively for a variety of applications ranging from biology to the environment [22-24]. Hydrogels offer several advantages over conventional methods. First, they are hydrophilic and are slightly higher than water [25,26]. Second, hydrogels can be synthesized with controllable sizes, charges and functional groups. Third, monomers with required functionalities are readily available for direct synthesis, eliminating the chemical treatments necessary to introduce functional groups to traditional absorbance [27,28]. Fourth, remove contaminants trough absorbing into their 3-D network providing more sites per unit volume.

Poly(3-acrylamidopropyl) trimethylammonium chloride hydrogels were utilized as absorbents for the removal of toxic arsenate from aqueous medium [29]. The mercaptyl resin, poly(ethylene mercaptoacetimide) (PEM), can remove arsenate and arsenite anions by redox sorption in acidic and alkaline media, respectively. The PEM resin prepared by the Schotten-Baumann reaction of polyethyleneimine with mercaptoacetyl chloride was determined to have a redox capacity of 8.26 meq/g dry resin [30]. Rivas *et al* investigated the new class of water soluble tin containing PAA matrix. Presumably, the Sn(II) ions coordinate through 2-4 carboxylate groups by a conventionally bidentate structure is applied to retain and separate arsenite from water [31]. A new hybrid adsorbent of titania–silica binary oxide-polyacrylonitrile (PAN) has been fabricated by loading nanosized sol–gel-derived $TiO_2$–$SiO_2$ onto a porous PAN polymer for enhanced As(III) and As(V) species removal from aqueous media. The prepared hybrid adsorbent exhibited highly selective arsenic retention from water in the presence of other ions at much greater levels than those toxic metals examined [32]. A Huge class of natural polymers and their derivative were frequently used for arsenite separation. Chitosan, chitin, chitosan/chitin mixture and their other modified derivative used for arsenic removal from contaminated drinking water [33-36].

It is well established that As(III) has a strong affinity toward mercaptan (thiol) groups existing in biomolecules such as amino acids, peptides and proteins (including some enzymes), which explains the higher toxicity of this species for human being [37-39]. Based on the above understanding, some thiol-based polymers including resins, adsorbents have been investigated by several authors [19,20,30,40-42]. These studies suggest that materials bearing thiol functional groups are very promising, and suitable alternate for specified As(III) removal. Based on the above fact it was thought worthwhile to synthesize new thiol-functionalized material for As(III) separation from water.

Polyvinyl alcohol (PVA) is a commercially available polymer that has been studied intensively in diverse areas of science technology development. The modification of PVA through its hydroxyl groups open new domains of applications in water treatment for this material (discussed in chapter 2). Few of PVA based materials are available in the literature. Polyvinyl alcohol mercaptyl fibers, coated on a fiber glass substrate, for the purpose of removing As(III) from water The fibrous mercaptyl system's performance is compared to the commercial product, Duolite's GT-73, a macroreticular polystyrene–divinylbenzene resin with chelating thiol functional groups [43]. Thiol-functionalized mesoporous PVA/$SiO_2$ composite nanofiber membranes were applied for the adsorption of heavy metal ions from aqueous solution [44].

The polymeric materials appears to be economically more feasible, due to the reused property of polymer. Three major methods for regeneration of the polymeric agent are known: Chemical, thermal and electrochemical regeneration methods. In this study, the chemical method has been used. By changing the pH of the environment, the polymer–metal complex bond is cleaved. The targated metal ions passed through the matrix [45]. Sudipta *et al* investigated the regeneration ability of ArsenX$^{np}$ is amenable to reuse for multiple cycles without any significant loss in removal capacity [46].

Addressing these problems calls out for a tremendous amount of research to be conducted to identify robust new methods for arsenic removal. At lower cost and with less energy, while at the same time minimizing the use of chemicals and impact on the environment. Here, we highlight some of the science and technology being developed to improve the coupled study on disinfection and arsenic removal. Vestergaard *et al* patented the water purification unit for killing microbes in water and arsenic removal. The unit comprises of different compartments with an iodine releasing resin for effective killing of microbes in water and arsenic removal [47]. In this research article, a novel PVA based chelating material bearing thiol groups were prepared by introducing esterification with thioglycolic acid and post crosslinking with sodiumtrimetaphophate onto the hydroxyl groups of the PVA under different conditions. The effects of several parameters pH, compositions of components and time on As(III) removal were examined. These optimized results were compared with As(III) removal experiments conducted with different water sample using crosslinked TPVA. The regeneration and antifungal ability of chelating material was also investigated.

## 5.2. Experimental

### 5.2.1. Materials

All chemicals were of analytical reagent grade or chemically pure grade and extra pure water, resistivity less than 18 MΩcm, produced by a Millipore Milli-Q system was used throughout the experimental work. Sodium arsenite ($NaAsO_2$, Impurity assay 0.001%) was supplied from Sigma and all metal salts were arranged from Merck, India ltd and were used as such.

### 5.2.2. Sources

As(III) stock solution (1000 ppb) was prepared by dissolving 0.174 g of $NaAsO_2$ in 100 mL of water. Working standard was prepared by appropriate dilution of stock. The different nature of water samples was used for the experiment.

### 5.2.3. Instruments

An Elico pH meter (model LI-127) was used for pH measurement. As(III) detection experiments were performed using a graphite furnace atomic absorption spectrometer equipped with a graphite tube (AAS-Perkins Elmer 3100). A hollow cathode lamp operated at a current of 8 mA and a wavelength of 193 nm with a spectral band width of 1 nm and deuterium background corrector was applied. All experiments were performed using a sample volume of 2 ml, injected by an auto sampler of GFAAS.

### 5.2.4. As(III) Removal Experiment

All the removal experiments were conducted by batch method. A known volume of As(III) solution was taken in 50 mL erlenmeyer flask was shaken with a desired dose of crosslinked TPVA for a specified contact time in a thermostated shaking assembly. After the predetermined contact time solution was filtered and the initial and equilibrium As(III) ion concentration in the aqueous solutions were analyzed by the atomic absorption spectrometry (AAS) method. The initial pH of the solutions was adjusted to the desired pH by adding 0.1 $\mathrm{molL^{-1}}$ HCl and NaOH solutions to the medium to maintain a constant pH. All experiments were performed in triplicate and mean values were presented in this study.

### 5.2.5. Regeneration Procedure

As(III) rich crosslinked TPVA was regenerated in a batch process at room temperature. The As(III)-rich chelated material (0.1 g) was equilibrated for an hour with 50 mL aliquots of 1 M regenerating solutions of different composition. Regenerating agents used included NaOH, $NaHCO_3$, HCl, $HNO_3$ and milliQ water. The best results were obtained using $HNO_3$ due to easy elution of As(III). It was further studied to optimize the concentration and contact time.

### 5.2.6. Antifungal Studies

Fungal strains used in the present study are C. Albicans (ATCC 90028). The clinical isolates were collected from the Department of Biosciences, Jamia Millia Islamia, New Delhi. All strains were grown on yeast extract 1% (w/v) peptone (2%) dextrose (2%) (YPD) medium. Cultures were maintained on YPD agar plates. The assays were carried out by colony count on incubated agar plates. The mixture of 0.5 ml of the cultured bacteria, 0.5 ml of the autoclaved sample solution and 4 ml of 0.05 M acetate buffer (pH 6.0) was incubated with shaking at 37 °C for 1 h. In control samples, 4.5 ml of the acetate buffer was used. The mixture solution (1 ml) was diluted by 10-fold, added to Tryptic soy agar (TSA, Difuco) medium, plated on a plastic petri-dish, and then incubated at 37 °C for 24 h. After incubation, the colonies were counted to indicate bactericidal activity which was calculated by the following equation:

$$\text{Bactericidal activity (\%)} = [(C-T)/C] \times 100 \qquad \textit{eq 1}$$

Where, $C$ is the colony numbers counted on the control and $T$ is those on the sample plate tested.

### 5.3. Results and Discussions

The experiments were focused on the removal of As(III) species by the use of thiol riched crosslinked TPVA. Batch experiments were applied to evaluate the As(III) removal performance of the chelating material. The schematic representation of removal mechanism is shown in Figure.5.1.

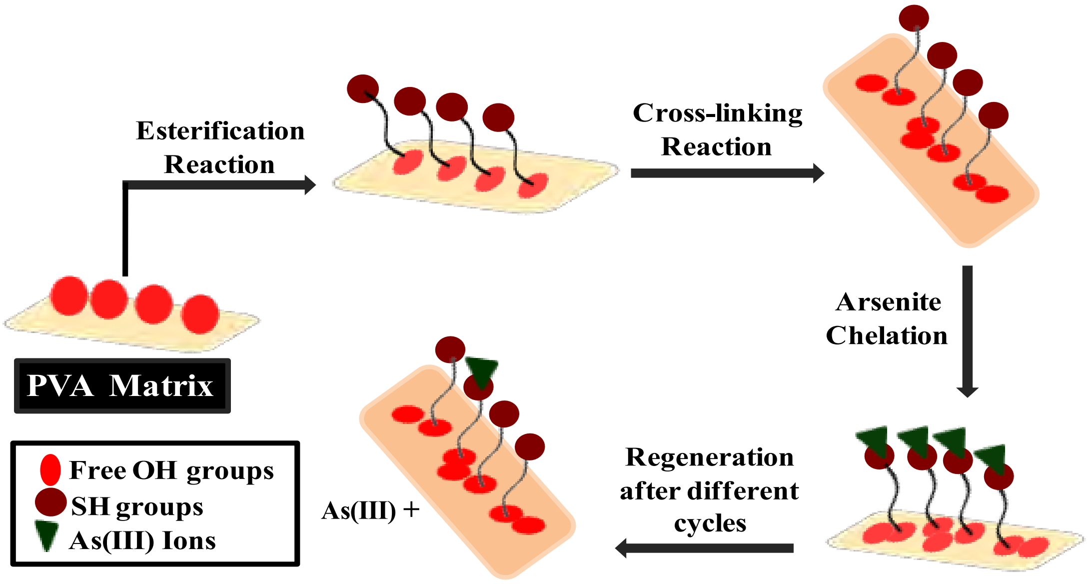


**Figure 5.1. Schematic representation of arsenite removal and regeneration process**

### 5.3.1. Influence of the Nature of Chelating Material

The results of removal experiments by different crosslinked chelating material presented in Figure 5.2 and Table 5.1. The results show that the crosslinked TPVA has consistently higher removal efficiency. The results obtained can be explained by observing the availability of functional groups for chelation in crosslinked TPVA. In the case of the crosslinked TPVA, thiol content is very high (3.5 mmol/g) and are predominantly responsible for the removal of As(III) ions. Removal efficiency is directly proportional to thiol content, as the thiol content increases more the chelating sites are available for As(III) binding. The fact the crosslinked TPVA has of 3-D network structure with good swelling ability which favors the contact between As(III) and thiol group and enhanced the removal efficiency.

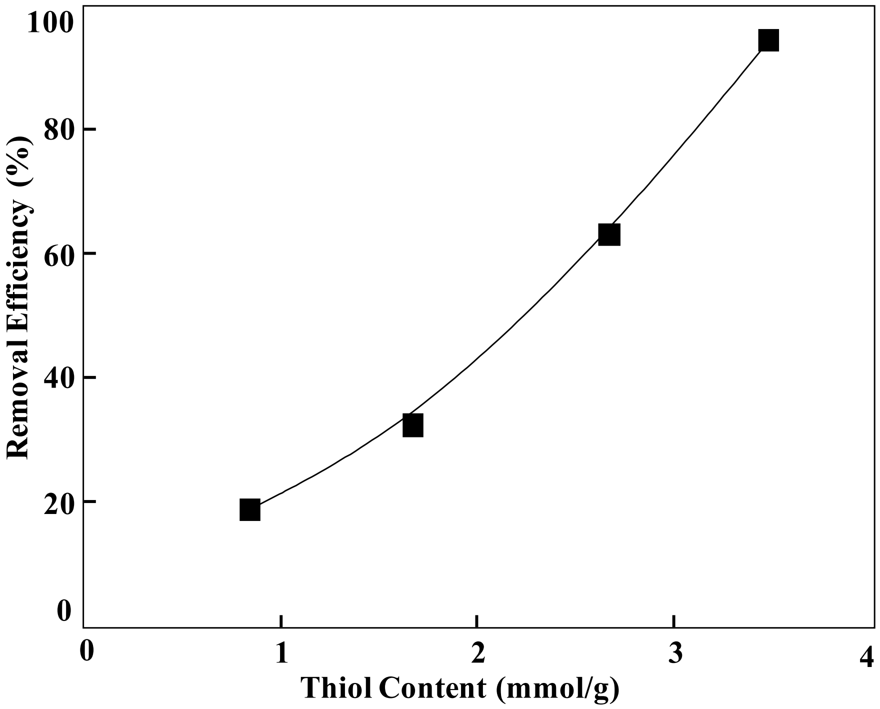


**Figure 5.2. Variation of the removal efficiency with the thiol content. Removal conditions: As(III), 100 ppb; pH, 7; TPVA wt, 2 g/L, contact time, 1 h**

**Table 5.1. Variation of the removal efficiency with the thiol content. Removal conditions: As(III), 100 ppb; pH, 7; TPVA wt,2 g/L; contact time, 1 h**

| **Thiol Content (mmol/g)** | **As(III) Concentration (ppb)** | **Removal Efficiency (%)** |
|---|---|---|
| 0.84 | 88.4 | 11.6 |
| 1.67 | 67.5 | 32.5 |
| 2.67 | 36.8 | 63.2 |
| 3.48 | 5.46 | 94.5 |

### 5.3.2. Influence of the Chelating Material Dose

The effect of TPVA dose on the removal of As(III) was studied at contact time of 1 h for initial As(III) concentration of 100 ppb. The results are presented in Figure 5.3 and Table 5.2, TPVA dose varied from 0.01-10 g/L. The removal efficiency of As(III) increased gradually with increasing amount of chelating material.

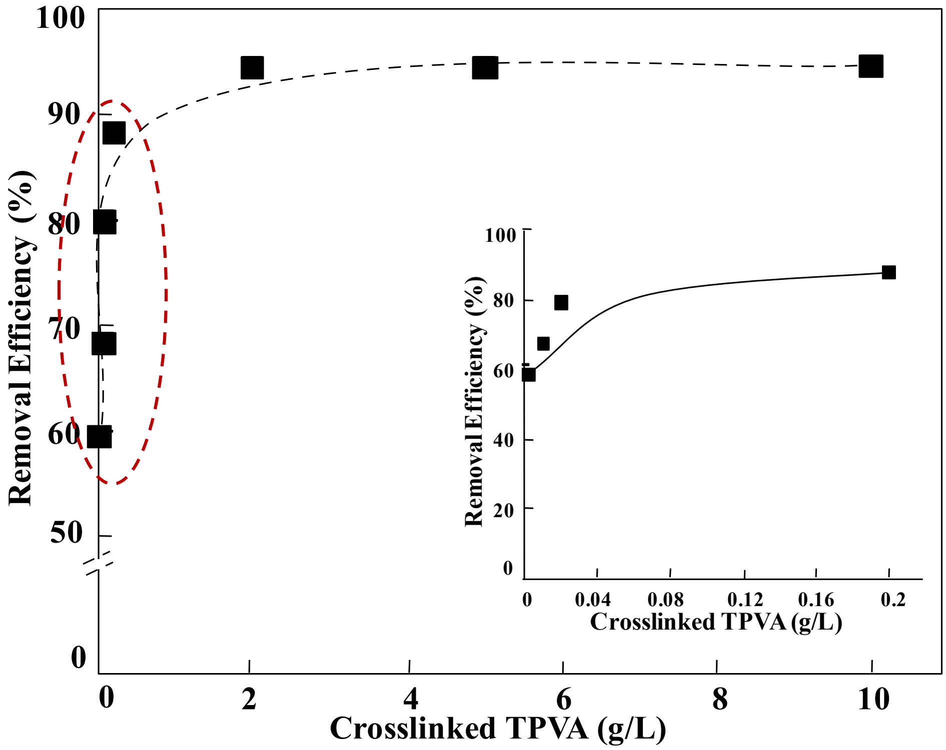


**Figure 5.3. Variation of the removal efficiency with the crosslinked TPVA. Removal conditions: Thiol conetnt; 3.5 mmol/g, As(III); 100 ppb, pH; 7, contact time; 1 h**

**Table. 5.2. Variation of the removal efficiency with the crosslinked TPVA. Removal conditions: Thiol content; 3.9 mmol/g, As(III); 100 ppb, pH; 7, contact time; 1 h**

| **XL-TPVA (g/L)** | **As(III) Concentration (ppb)** | **Removal Efficiency (%)** |
|---|---|---|
| 0.002 | 59.3 | 56.2 |
| 0.01 | 68.2 | 63.8 |
| 0.02 | 20.2 | 79.8 |
| 0.1 | 17.8 | 82.2 |
| 0.2 | 11.8 | 88.3 |
| 1 | 8.2 | 91.8 |
| 2 | 5.5 | 94.5 |
| 5 | 5.5 | 94.5 |
| 10 | 5.5 | 94.5 |

The removal efficiency of material depends on the active sites that is the specifically available for the As(III) chelation. However, it is observed that after dosage of 2 g, there was no significant change in removal of As(III). It may be due to the formation of agglomeration of the chelating material themselves at higher dosage. Therefore, the removal efficiency was not increased with the dose of material. Hence, 2 g/L was taken as optimum dose and used for further study.

### 5.3.3. Influence of the Contact Time

Variation of As(III) removal efficiency with contact time is presented in Figure 5.4 and Table 5.3. Removal of As(III) at different contact time was studied for initial concentration of 100 ppb, keeping all other parameters constant. It is clear from the plot, that 94.5% removal took place within 1 h and equilibrium was established after 2 h. The change in the rate of removal might be due to the fact that initially all chelating sites were vacant and the solute concentration gradient was high.

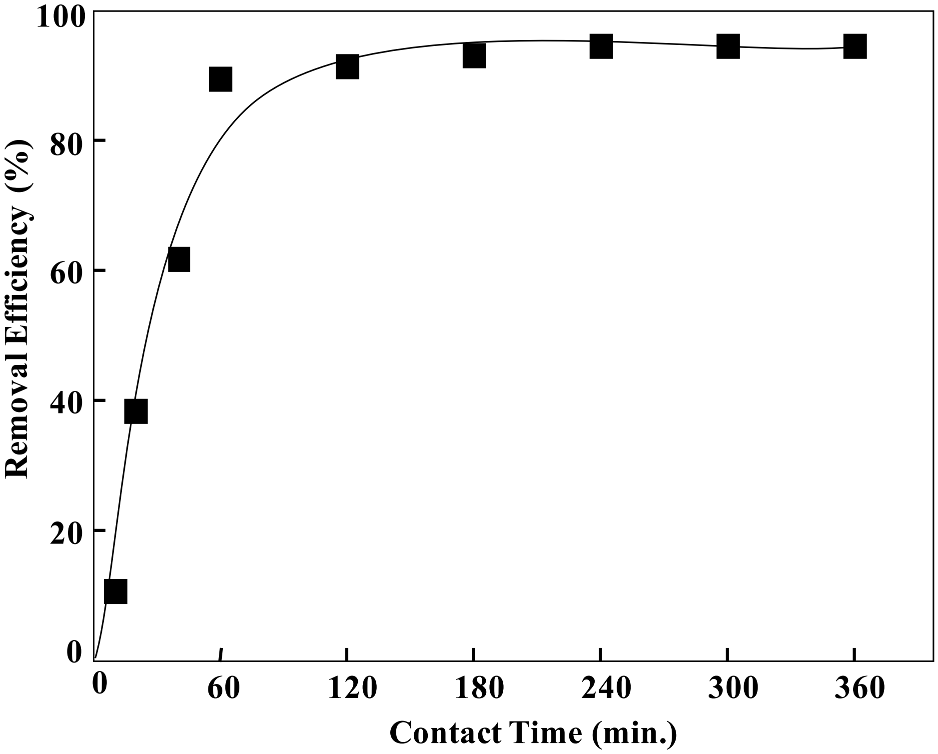


**Figure 5.4. Variation of the removal efficiency with the contact time. Removal conditions: As(III), 100 ppb; pH, 7; TPVA wt, 2 g/L**

**Table 5.3. Variation of the removal efficiency with the contact time. Removal conditions: As(III), 100 ppb; pH, 7; TPVA wt, 2 g/L**

| Contact Time (min) | As(III) Concentration (ppb) | Removal Efficiency (%) |
|---|---|---|
| 20 | 41.8 | 58.2 |
| 40 | 10.5 | 89.5 |
| 60 | 5.5 | 94.5 |
| 120 | 5.5 | 94.5 |
| 180 | 5.5 | 94.5 |
| 240 | 5.5 | 94.5 |

The As(III) uptake efficiency by chelating material was decreased significantly, due to the unavailability of vacate sites in TPVA after certain time interval.

### 5.3.4. Influence of the As(III) Concentration

The removal efficiency is highly dependent on the initial concentrations of As(III) in the feed water. The initial concentration was evaluated in the range of 10 to 1000 ppb and the results were illustrated in Figure 5.5 and in Table 5.4. The removal efficiency decreased with increasing of initial concentration of As(III). In most of the affected areas the contamination range is ~100ppb.

**Table 5.4. Variation of the removal efficiency with the As(III) concentration in feed water. Removal conditions: Contact time, 1 h; pH, 7; TPVA wt, 2 g/L**

| Initial As(III) Concentration (ppb) | As(III) Concentration (ppb) | Removal Efficiency (%) |
|---|---|---|
| 10 | 4.8 | 95.2 |
| 50 | 5.4 | 94.6 |
| 100 | 5.5 | 94.5 |
| 500 | 25.7 | 74.3 |
| 1000 | 47.2 | 52.8 |

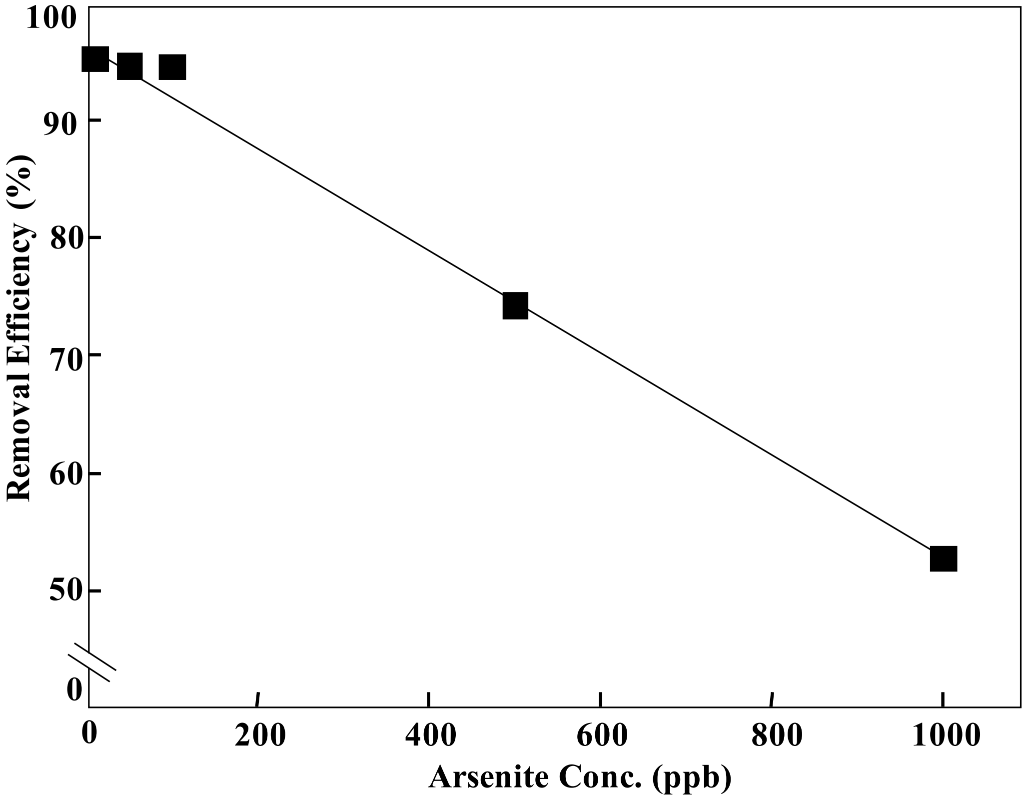


**Figure 5.5. Variation of the removal efficiency with the As(III) concentration in feed water. Removal conditions: Contact time, 1 h; pH, 7; TPVA wt, 2 g/L**

From this experiment, it is observed that constant removal efficiency was achieved using 100 ppb of As(III) solution. These phenomena might be due to the fact that at low concentration, most of the As(III) in the solution might rapidly chelate with TPVA. Therefore, a sequencing could be used for commercialized product, the present study tha batch method is taken into consideration.

### 5.3.5. Influence of the pH

The complexation of As(III) ions by a chelating ligand strongly depends on pH. The medium pH affects both the solubility of metal ion and the protonation state of the donating groups of the chelating material. Removal efficiency of As(III) was studied at contact time of 1 h for initial As(III) concentration of 100 ppb at different pH. The results are presented in Figure 5.6 and Table 5.5. The efficiency curve was an essentially hump shape in the pH range 4-10, and then the efficiency tended to decreases in basic medium. Under the most acidic condition (pH 2-5) as well as in basic condition (pH 9-14) the removal efficiency of As(III) was very low. This is because that chelating material underwent a fast hydrolysis of their ester linkage. It is evident that the highest removal efficiency was achieved at pH 7.

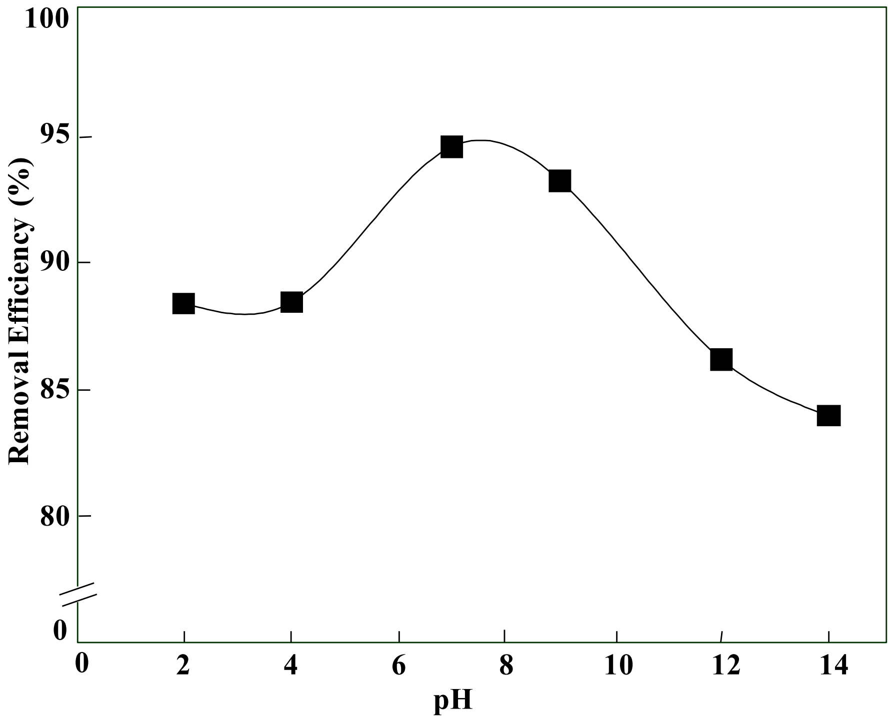


**Figure 5.6. Variation of the removal efficiency with the different pH media. Removal conditions: Contact time, 1 h; TPVA wt, 2 g/L, As(III), 100 ppb**

**Table 5.5. Variation of the removal efficiency with the different pH media. Removal conditions: Contact time, 1 h; TPVA wt, 2 g/L, As(III), 100 ppb**

| pH | As(III) Concentration (ppb) | Removal Efficiency (%) |
|---|---|---|
| 2 | 11.6 | 88.4 |
| 4 | 11.6 | 88.4 |
| 7 | 5.5 | 94.5 |
| 9 | 6.8 | 93.2 |
| 12 | 13.8 | 86.2 |
| 14 | 16.0 | 84.0 |

This result should be great advantage for the practical implementation of arsenic removal from ground, surface and drinking water.

### 5.3.6. Influence of the Competitive Ions

Drinking water contains many other salts such as sodium bicarbonate, magnesium sulfate, sodium chloride and calcium chloride along with As(III), which may compete with As for the active chelation site. In order to study the effect of competitive ions, the removal studies were carried out in the presence of salts solutions of various ions at different concentration ppb. The experimental conditions for As(III) concentration was kept at 100 The global median values of surface water concentrations were used for bicarbonate 58 ppm and chloride 8.7 ppm maximum contaminant level (MCL) in drinking water was used [48].

Calcium is largely responsible for water hardness and may interfere with the separation efficiency of the material. In Figure 5.7 and Table 5.6, we have observed the effect of calcium chloride on As(III) removal efficiency. The influence of calcium ions (10 to100 ppm) on the arsenic removal efficiency was investigated using a model solution containing the concentration range corresponding to those present in tap water. It was found that the presence of Ca ions have limited effects on As(III) removal. In addition, for the groundwater with high hardness, presence of Ca ions promote the removal process.

Sodium bicarbonate, magnesium sulfate and sodium chloride salts in water are considered other competing ions in the As(III) removal process represented in Figure 5.8, 5.9, 5.10 and Table 5.7, 5.8, 5.9 respectively. From the removal experiments results, it was observed that $CaCl_2$, $HCO_3^-$ and $MgSO_4$ shows negative effects on removal of As(III).

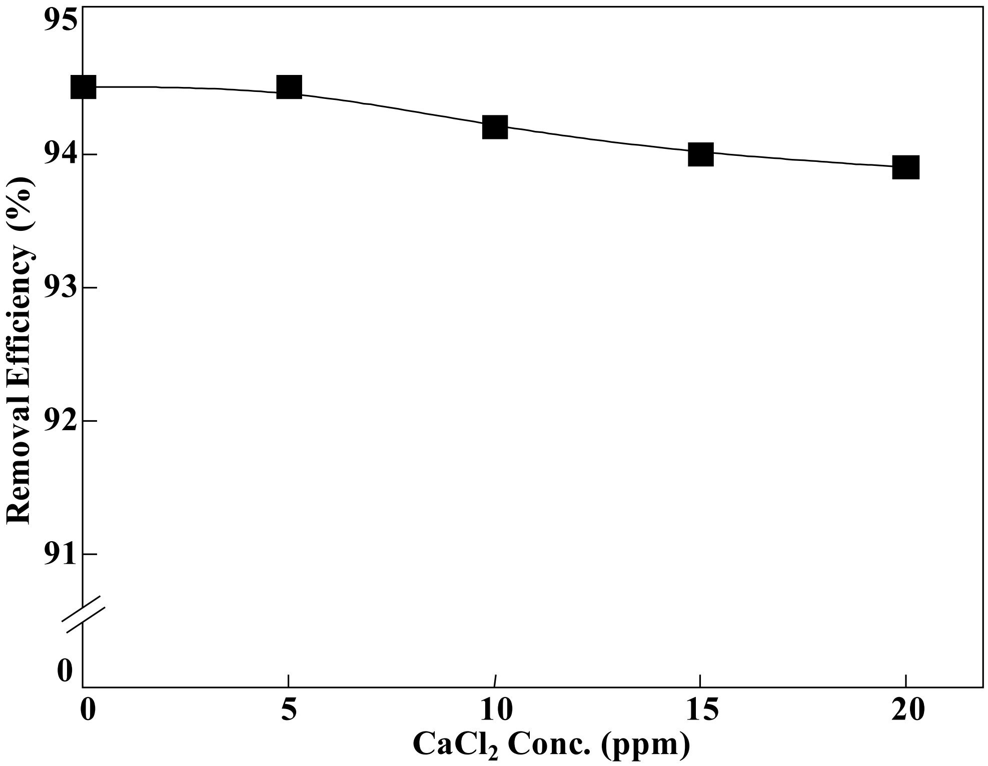


Figure 5.7. Variation of the removal efficiency with the $CaCl_2$ concentration. Removal conditions: contact time, 1 h; TPVA wt, 2 g/L, As(III), 100 ppb

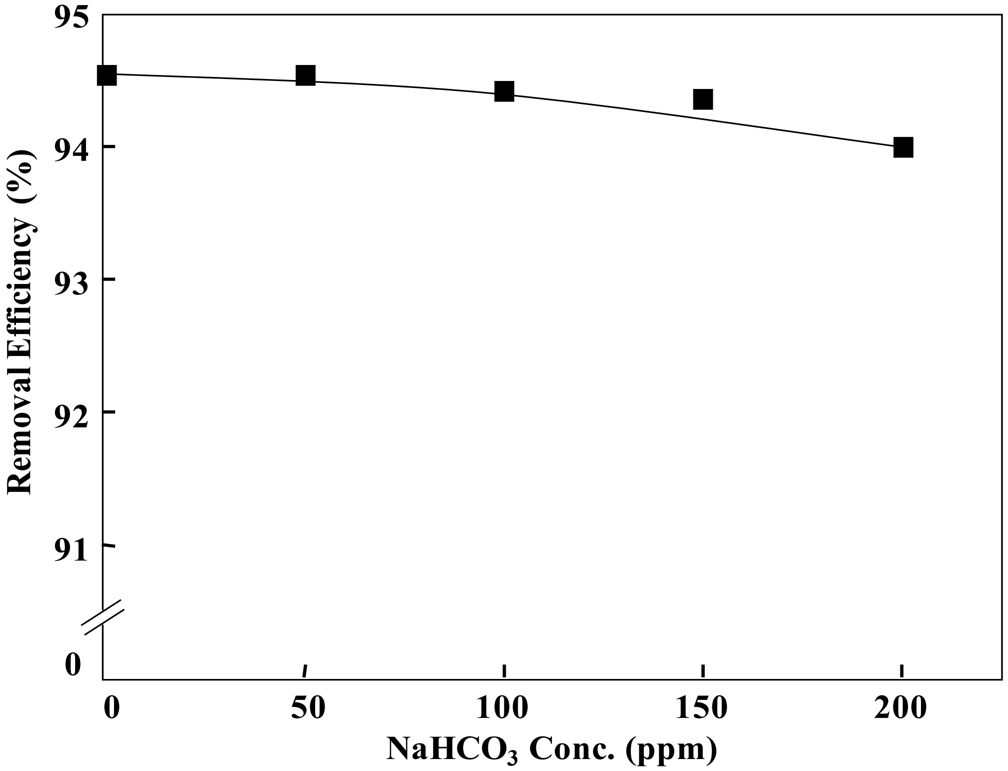


Figure 5.8. Variation of the removal efficiency with the varying $NaHCO_3$ concentration. Reaction conditions: Contact time, 1 h; TPVA wt, 2 g/L; As(III), 100 ppb

**Table 5.6. Variation of the removal efficiency with the $CaCl_2$ concentration. Removal conditions: contact time, 1 h; TPVA wt, 2 g/L; As(III), 100 ppb**

| $CaCl_2$ Conc (ppm) | Initial As(III) Conc (ppb) | As(III) Conc (ppb) | Removal Efficiency (%) |
|---|---|---|---|
| 0 | 100 | 5.5 | 94.5 |
| 5 | 100 | 5.5 | 94.5 |
| 10 | 100 | 5.8 | 94.2 |
| 15 | 100 | 5.9 | 94.0 |
| 20 | 100 | 6.1 | 93.9 |

**Table 5.7. Variation of the removal efficiency with the varying $NaHCO_3$ concentration. Reaction conditions: Contact time, 1 h; TPVA wt, 2 g/L, As(III), 100 ppb**

| $NaHCO_3$ Conc (ppm) | Initial As(III) Conc (ppb) | As(III) Conc (ppb) | Removal Efficiency (%) |
|---|---|---|---|
| 0 | 100 | 5.4 | 94.6 |
| 50 | 100 | 5.5 | 94.5 |
| 100 | 100 | 5.5 | 94.5 |
| 150 | 100 | 5.6 | 94.4 |
| 200 | 100 | 5.6 | 94.4 |

**Table 5.8. Variation of the removal efficiency with the varying $MgSO_4$ concentration. Removal conditions: Contact time, 1 h; TPVA wt, 2 g/L; As(III), 100 ppb**

| $MgSO_4$ Conc (ppm) | Initial As(III) Conc (ppb) | As(III) Conc (ppb) | Removal Efficiency (%) |
|---|---|---|---|
| 0 | 100 | 5.5 | 94.5 |
| 2 | 100 | 5.4 | 94.5 |
| 4 | 100 | 5.5 | 94.5 |
| 6 | 100 | 5.6 | 94.4 |
| 8 | 100 | 5.6 | 94.4 |

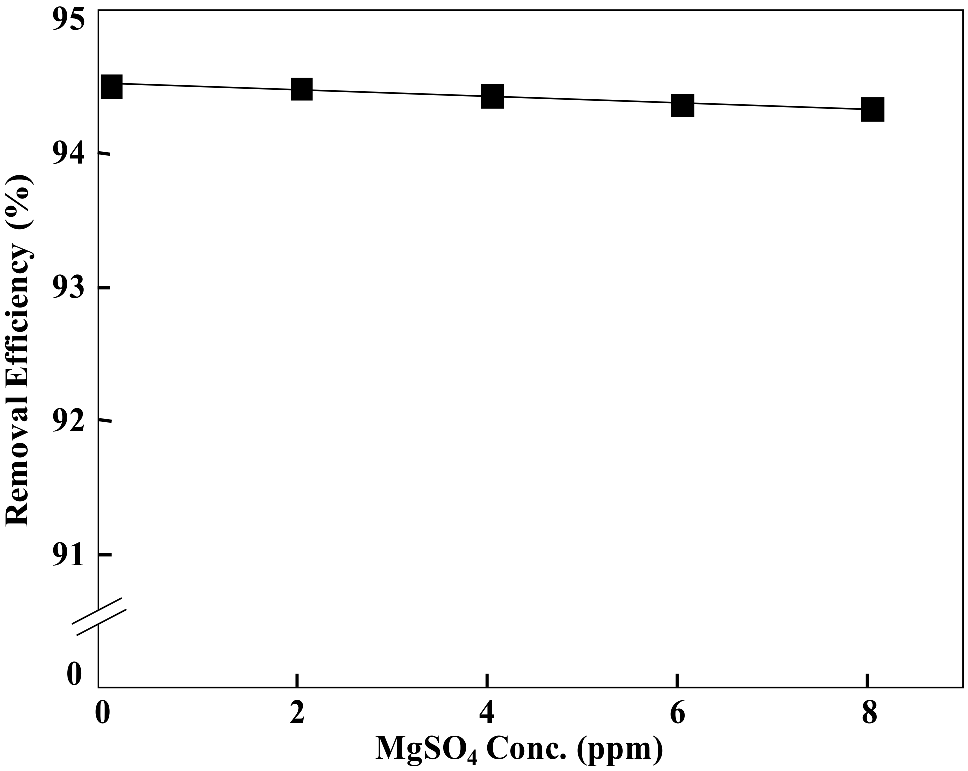


Figure 5.9. Variation of the removal efficiency with the varying $MgSO_4$ concentration. Removal conditions: Contact time, 1 h; TPVA wt, 2 g/L; As(III), 100 ppb

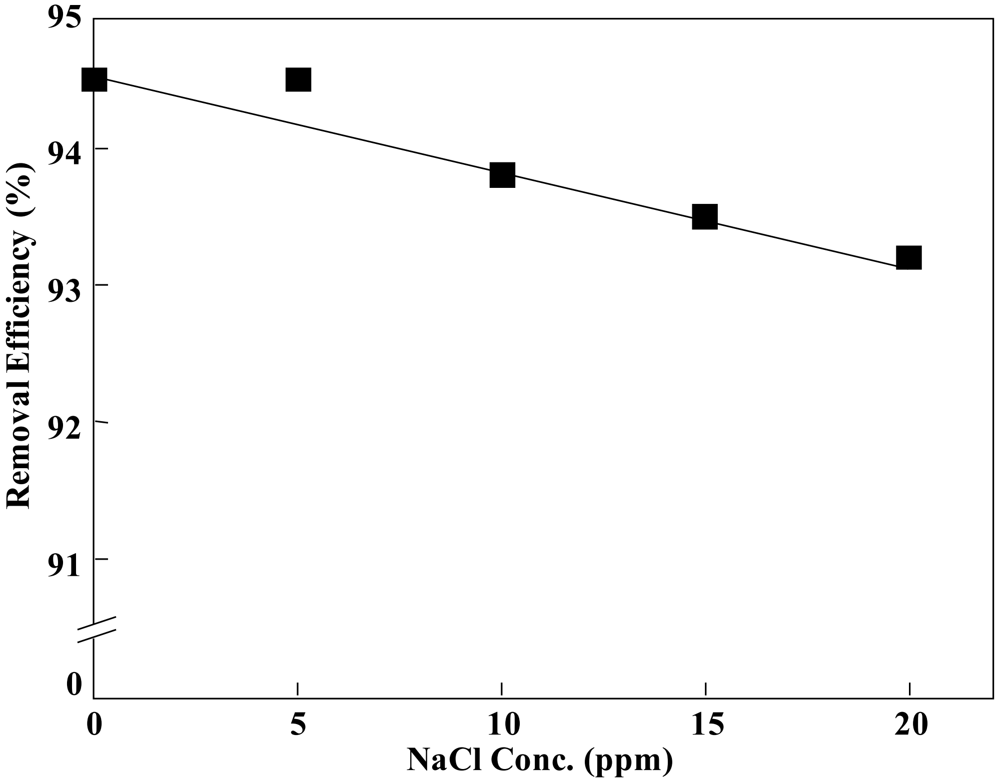


Figure 5.10. Variation of the removal efficiency with the varying NaCl concentration. Reaction conditions: Contact time, 1 h; TPVA wt, 2 g/L, As(III), 100 ppb

**Table 5.9. Variation of the removal efficiency with the varying NaCl concentration. Removal conditions: Contact time, 1 h; TPVA wt, 2 g/L; As(III), 100 ppb**

| NaCl Concentration (ppm) | Initial As(III) Concentration (ppb) | As(III) Concentration (ppb) | Removal Efficiency (%) |
|---|---|---|---|
| 0 | 100 | 5.5 | 94.5 |
| 5 | 100 | 5.5 | 94.5 |
| 10 | 100 | 6.2 | 93.8 |
| 15 | 100 | 6.5 | 93.5 |
| 20 | 100 | 6.8 | 93.2 |

However, the experiment results showed that the presence of NaCl showed lesser As(III) removal. The pH of As(III) solution was higher than 7 while the pH of the solution was neutral without addition of any salts. This indicates that additions of salts resulted in an increased pH of As(III) solutions. From our experiments on the effect of pH (Section 5.3.5) it was observed that the removal of As(III) decreases in alkaline pH as also explained. As mentioned before, in this study the -SH group in crosslinked thiolated PVA is predominantly responsible due to the high affinity toward the chelation of As(III). The sulfur present in the thiol group has inactivity towards the non target metal ions which were used in this study. This is one of the possible reasons why the competitive anion does not have a bearing on arsenic removal.

### 5.3.7. Influence of the Nature of Water Sample

Arsenic chelation was greatly affected by the quality of the water, the pH of the water and the speciation of arsenic itself. As(III) removal efficiency in the different nature of the sample was shown in Figure 5.11. The initial As(III) concentration of 100 ppb was reduced to 5.4 ppb (94.5% removal efficiency). Interestingly, the nature of water did not influence the As(III) removal efficiency. The determination of the As(III) in the samples presented in Table 5.10 showed different levels of arsenic samples (MiliQ and mineral water) had about 1ppb, but the other samples (tap water) contained higher amounts. The recovery and reproducibility of laboratory blank and spiked samples were good. No interference effects were observed in the natural water samples.

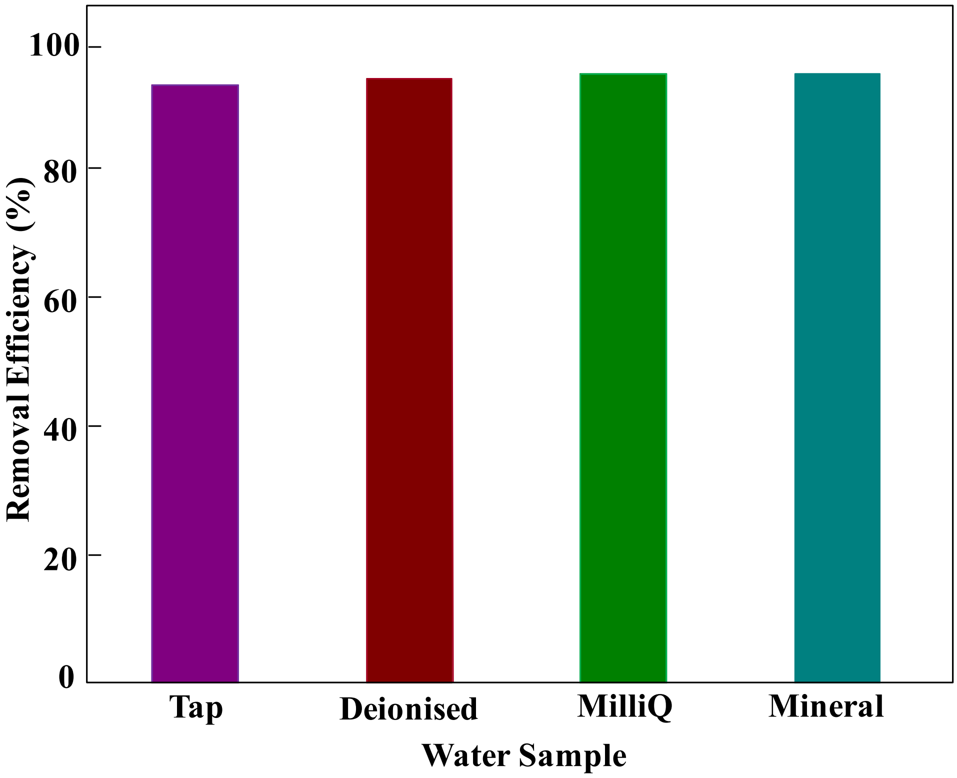


**Figure 5.11. Variation of the removal efficiency with the different water sample. Removal conditions: Contact time, 1 h; TPVA wt, 2 g/L; As(III), 100 ppb**

**Table 5.10. Variation of the removal efficiency with the different water sample. Removal conditions: Contact time, 1 h; TPVA wt, 2 g/L; As(III), 100 ppb**

| **Sample** | **As(III) (ppb)** | **Total As(III) (ppb)** | **Removal Efficiency (%)** |
|---|---|---|---|
| Tap water | 100 | 115 | 92.9 |
| De-ionized water | 100 | 104 | 93.8 |
| Mili Q water | 100 | 101 | 94.5 |
| Mineral Water | 100 | 101 | 94.5 |

With this simple procedure, analysts obtain a good insight into the status of arsenic species in water samples.

### 5.3.8. Regeneration Process of Crosslinked TPVA

Regeneration and reuse of chelating material carries utmost importance, which directly affects the cost factor and hence its utility in the continuous batch removal process. The polymer based chelating materials that can be reused have practical value in real system. In order to determine the reusability of the crosslinked TPVA the removal and regeneration process was repeated several times. As can be seen from the Figure 5.12 and Table 5.11 the use of crosslinked TPVA has a slightly less removal efficiency after different cycles. However, it may be possible to regenerate the chelating material by various treatments.

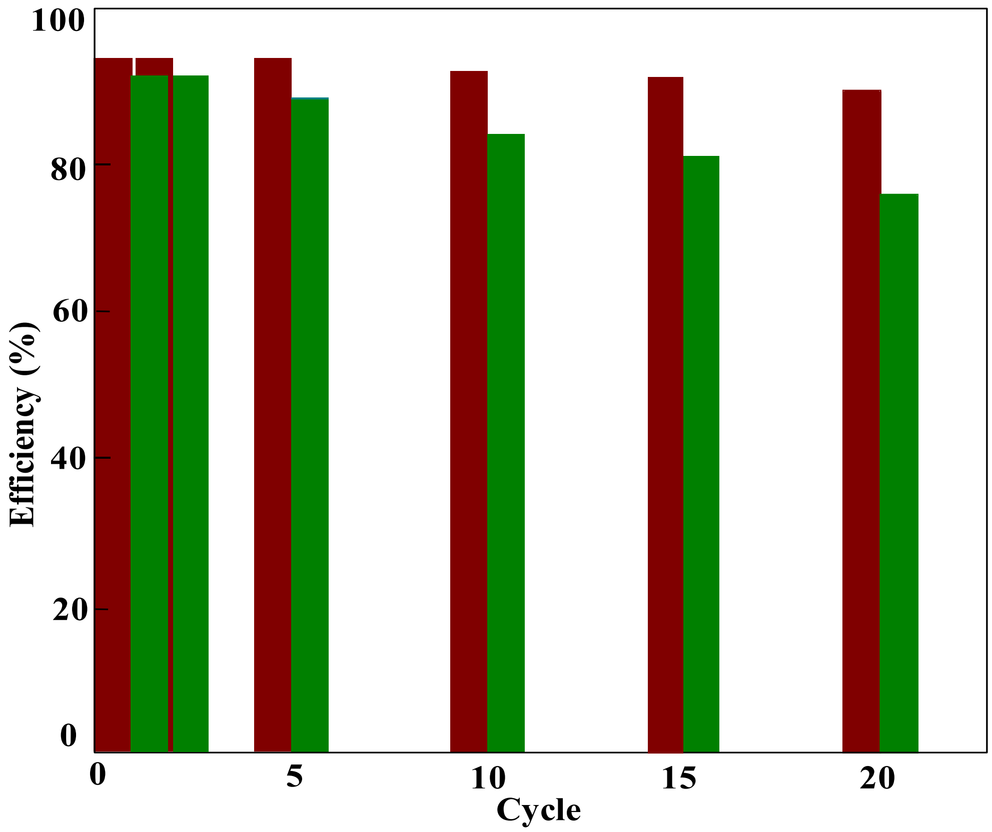


**Figure 5.12. Variation of the removal efficiency with the regeneration cycle. Reaction conditions: Reagent, $HNO_3$; contact time, 2 h; Removal efficiency 🟥Regeneration efficiency 🟩**

**Table 5.11. Variation of the removal efficiency with the regeneration cycle. Reaction conditions: Reagent, $HNO_3$; contact time, 2 h**

| Cycle | Removal Efficiency (%) | Regeneration (%) |
|---|---|---|
| 1 | 94.5 | 92 |
| 2 | 94.5 | 92 |
| 5 | 94.5 | 89 |
| 10 | 92.7 | 84 |
| 15 | 92 | 81 |
| 20 | 90 | 76 |

The arsenite riched crosslinked TPVA membrane has been used for the regeneration process by different solution media in various conditions shown in Figure 5.13 and Table 5.12.

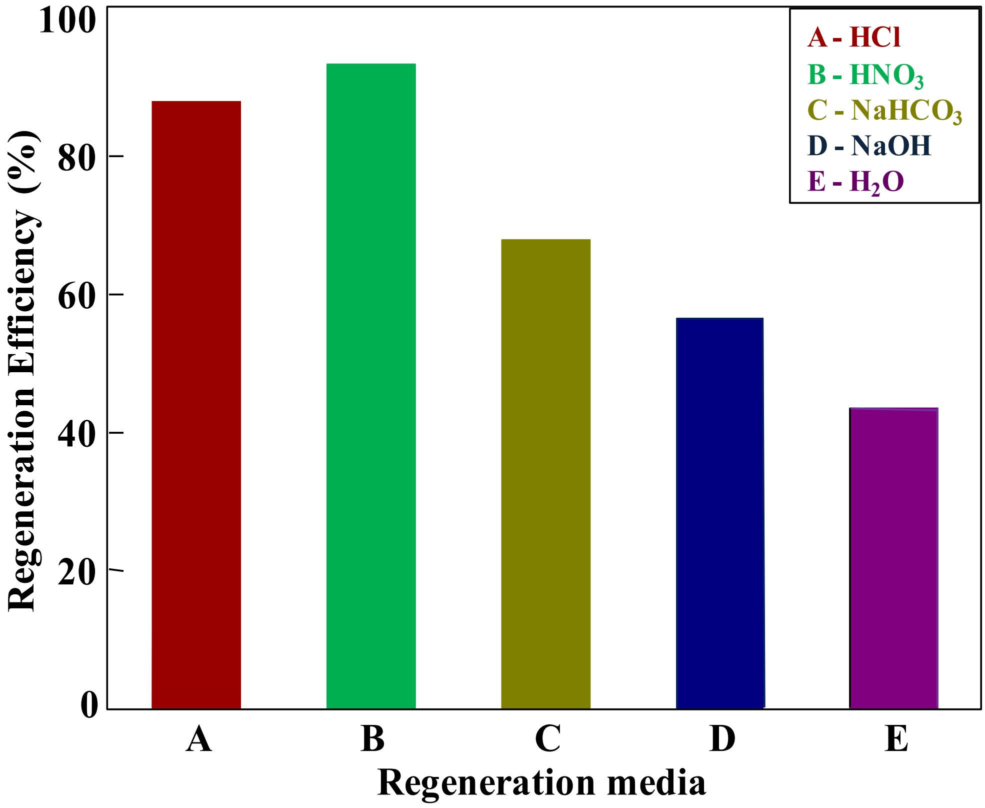


**Figure 5.13. Variation of the regeneration efficiency under different media. Reaction conditions: Contact time, 2 h**

**Table 5.12. Variation of the regeneration efficiency under different media. Reaction conditions: Contact time, 2 h**

| Media | As(III) (ppb) | Regeneration (%) |
|---|---|---|
| HCl | 11.6 | 88.4 |
| $HNO_3$ | 5.5 | 94.5 |
| $NaHCO_3$ | 29.7 | 70.3 |
| NaOH | 41.3 | 58.7 |
| $H_2O$ | 54.4 | 45.6 |

Different regenerating agents tested included, HCl. $HNO_3$, $NaHCO_3$. Although the achievement of As(III) elution using strong acidic or alkaline solutions has been reported in the literature [49]. The present work showed that effective desorption was obtained with acid solutions. Desorption of As(III) was very poor in the alkaline media., NaOH and Milli Q water have been used for elution of chelated As(III) from crosslinked TPVA at various conditions. During this experiment, the addition of alkaline into crosslinked TPVA causes a fast ester hydrolysis.

The influence of contact time on regeneration efficiency is presented in Figure 5.14 and Table 5.13.

**Table 5.13. Variation of the regeneration efficiency with the contact time. Reaction conditions: Reagent, $HNO_3$**

| Contact Time (min) | As(III) (ppb) | Regeneration (%) |
|---|---|---|
| 30 | 42.0 | 58.0 |
| 60 | 22.7 | 77.3 |
| 90 | 9.6 | 90.4 |
| 120 | 5.5 | 94.5 |
| 150 | 5.5 | 94.5 |
| 180 | 5.5 | 94.5 |

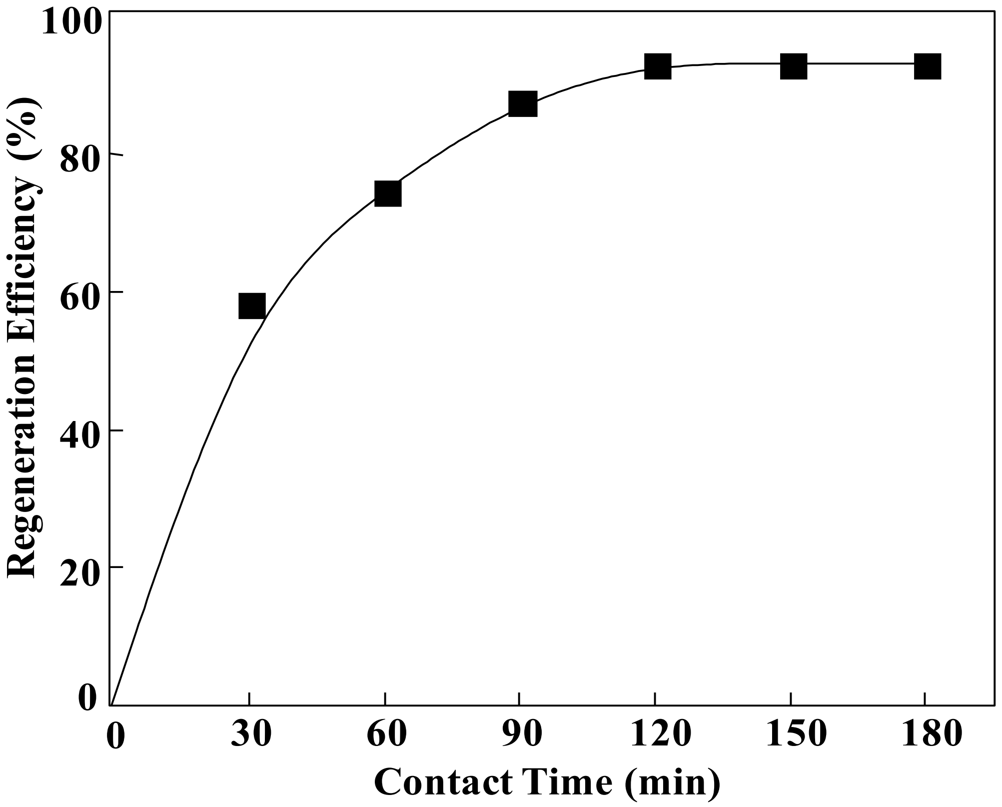
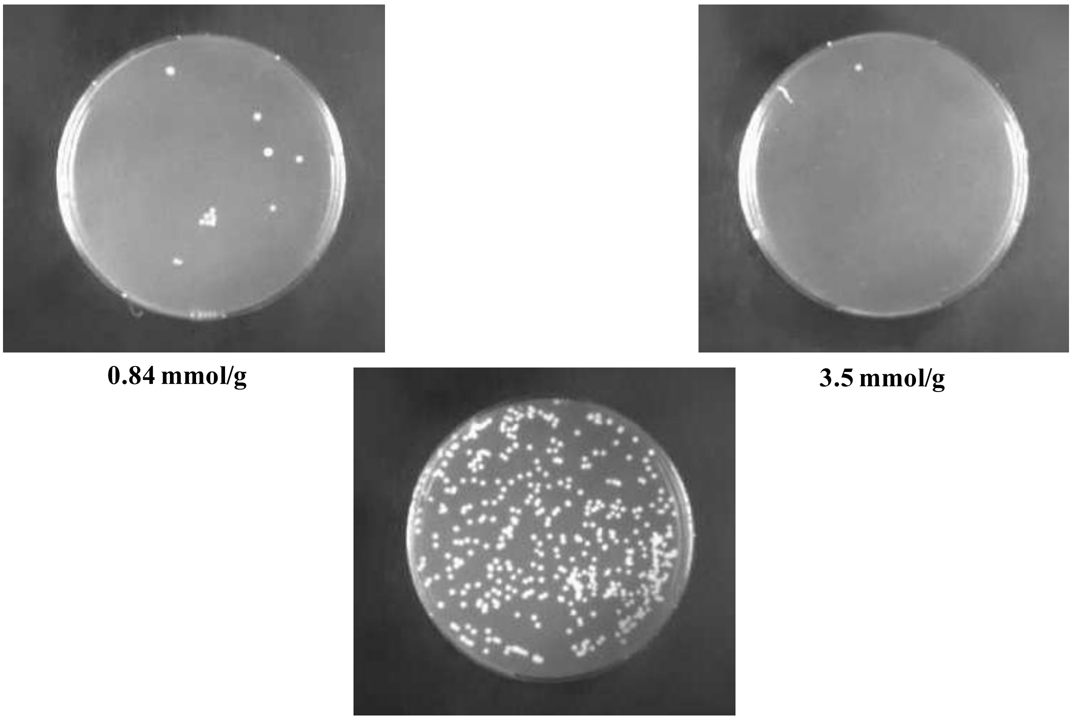


**Figure 5.14. Variation of the regeneration efficiency with the contact time. Reaction conditions: Reagent, $HNO_3$**

In general, the regeneration efficiency of As(III) tended to increase with increasing desorption time. Consequently, acid solution was useful for desorption of arsenic from the crosslinked TPVA matrix.

### 5.3.9. Antifungal Studies of Crosslinked TPVA

The main problem in any material application for water treatment is fouling which is used in the separation process due to the long contact time with water. The consequence is obvious and includes pretreatment in any process. The present investigation focuses on the development of good anti-fouling crosslinked TPVA-based arsenite chelating material. The derived material (TPVA) having active thiol groups were crosslinked to ionic crosslinker STMP. The resulting material has excellent anti fungal properties because of the ionic crosslinker STMP (good anti fouling agent). The CFU images of different material against a standard strain of *Candida Albicans* are shown in Figure 5.15.



**0.84 mmol/g**

**3.5 mmol/g**

**Pure PVA**

**Figure 5.15. CFU images of pure PVA and different TPVA samples against standard strain of Candida Albicans**

Contaminated water contains pathogens (bacteria, fungus and virus) it can occur in water derived from groundwater, rainwater, or surface water. Therefore, the strong need is required to regulate the presence of pathogens with arsenic removal. The couple material is quite supportive for this issue.

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# Chapter 6

# CONCLUSION

## 6. Summary

The first chapter reviewed the precise information on arsenic crisis and different technologies used for detection and the removal of arsenic from water in various levels.

Chapter II deals with the simple esterification reaction of polyvinyl alcohol (PVA) with thioglycolic acid (TGA) in presence of catalyst which offers an attractive route to develop thiol content in base material. The esterification reaction was carried out using mineral acid ($H_2SO_4$) as a homogeneous catalyst in the reaction medium for the enhancement of reactivity of components. It was observed that the esterification is significantly influenced by the reaction conditions, such as reaction time, temperature, alcohol, acid and catalyst concentration. However, as all parameters increases a sharp acceleration was observed in thiol content due to the proper interaction between the presenting groups of acid and alcohol. The calculated thiol content is directly proportional to the acid and catalyst concentration, reaction time and temperature. The reaction could not be carried out beyond 2% PVA concentration and higher temperature due to gelation. Thiol content in modified PVA was found to increase with the reaction time, therefore the optimized reaction time is 24 h. The increase in the acid and catalyst concentration leads to the increase in the resulting thiol content at 25% and 1% respectively.

The most interesting aspect of the esterification process is that the reaction temperature effect on the contribution of strong in-situ interaction in modified PVA matrix. The thiol content was found to be very high at 60 °C above which it decreases. As a result the hydroxyl groups of PVA are condensed and lead to lower thiol content. The swelling data decreases with increasing reaction temperature at optimized acid and catalyst concentration. The structural changes of the thiolated PVA were found to depend on the thiol content and confirmed with Attenuated total reflection- Infrared spectroscopy (ATR-IR). Therefore suitable thiol content as well as properties can be achieved in the modified PVA via proper selection of the reaction conditions.

Chapter III deals with the crosslinking of derived thiolated PVA with different nature of crosslinker at various influenced parameters. As is well known, the mechanics and stability of pure PVA material without further crosslink can break down due to low wet stability. Crosslinking of PVA is highly interesting domain to introduce desirable property and enhance the used in various further applications. Previously derived TPVA have been post cross-linked by using different crosslinking reagents i.e. sodium trimetaphosphate (STMP), boric acid (BA), glyoxal (GLY), under alkaline conditions. The effects of the different crosslinking reagents on the physicochemical and structural characteristics of crosslinked thiolated PVA were evaluated. The three reagents used for crosslinking presented different action mode on TPVA at various condition. The crosslinking reaction was carried out at different conditions i.e. TGA concentration, crosslinker nature, crosslinker content and crosslinking time, resulting sample was showing inverse relation with thiol content and swelling studies. The swelling studies have been carried out at different interval of time and various pH media

All physicochemical and structural study showed that the STMP crosslinked TPVA had the lowest crosslinking density as to others and suitable for further use. The optimized crosslinking conditions were observed that crosslinker time of 30 min at 0.1% crosslinker content. The structural changes of the crosslinked TPVA were found to depend on the thiol content and swelling studies. The crosslinking action and structural change in the modified matrix have been confirmed by Attenuated total reflection- Infrared spectroscopy (ATR-IR) due to the presence of characteristic peaks. Therefore after crosslinking the thiol content value become decreases due to inhibitory interaction of water with PVA as well as properties can be achieved in the modified PVA via proper selection of the reaction conditions.

Chapter IV deals with the characterization of virgin and modified PVA. Most of the modifications of PVA have been performed with reactions with the pendent hydroxyl groups of PVA because of the high reactivity of hydroxyl groups. However, the number of hydroxyl groups of PVA would certainly decrease after the aforementioned modification. Consequently, some desirable characteristics and properties of PVA might vanish or abate. Various conditions, like reaction time, reaction temperature, reactants concentration, nature of crosslinkers, crosslinker content and crosslinking time were optimized in above section. In this state-of-art, we have attempted to characterize the structural changes obtained by two step modification in PVA. The crosslinked TPVA films have been characterized by TGA, DSC, XRD, FTIR and coupled TG-FTIR techniques. A significant variation in the initial decomposition temperature (IDT), crystallinity and evaluation of components were observed with respect to different STMP crosslinked samples having varying TGA concentration and different crosslinkers. The influence of the esterification and crosslinking on the physical structure of the material was studied through different techniques.

The TGA results showed that the thermal stability of PVA films increased after simultaneous modification. The IDT of STMP crosslinked TPVA were increased with increasing STMP content due to the crosslinking. DSC thermograms of crosslinked films showed the appearance of single melting thermograms. After thiolation of PVA, the $T_g$ decreases due to the formation of strong covalent bond while after crosslinking the $T_g$ value increases due to the diminishing degree of crystallinity. On the other hand, crosslinking of TPVA with STMP disappears the quasi-crystalline phase due to the involvement of free hydroxyl groups which remain after esterification in the crosslinking process. The XRD scans for the modified PVA there were two peaks at 2θ = 14 and 16º which revealed a PVA crystal structure. With increasing TGA concentration at same crosslinker content however, the first peak disappears and second gradually shifted toward 2θ = 19°, indicated the distraction of a crystalline nature after simultaneous modification. The crystalline reflections for STMP crosslinked TPVA were found to occur at distinct angles.

For the variation in different crosslinker at optimized crosslinking conditions, the characteristic properties were also been discussed by various characterization. The XRD studies reveals that different crosslinker shows distinct nature like another two crosslinker shows more crystalline nature as comparison with STMP. In our case all three crosslinker STMP, BA, GLY created the bridges between the polymer chains which are not rigid ones, but flexible sequences of phosphate, borate and acetal formation, respectively. The DSC studies show a rapid decrease of the heat of fusion ΔH and melting temperature $T_m$ and testify to the diminution of crystallinity with crosslinking. This may be since due to the binding of PVA chains which restricts the arrangement of chains due to of crystal structure.

The coupled TG-FTIR studies of crosslinked samples were used for the analysis of the evolved gases from material at different temperature. To compare the evolved gases of the samples, the FTIR spectra in the region below 200 °C, about 275 °C, 385 °C and 470 °C are studied with the most relevant reference substances from the NIST database. most important representation of this spectrogram is to show the evolution of sulfur containing gaseous being prominent for this material. The $CS_2$ evolution is investigated at 1575 – 1500 $cm^{-1}$ and the liberation of COS is observed at 2150 – 2050

$cm^{-1}$. With respect to the TGA-FTIR spectra the present study was not able to detect $H_2S$, $SO_2$ and any other relevant sulfur containing gas.

Chatpter V deals with the application of novel PVA based chelating material bearing thiol groups for arsenite removal from water. Batch experiments were applied to evaluate the As(III) removal performance of the chelating material. The effects of several parameters pH, compositions of components and contact time for As(III) removal were examined. Atomic absorption spectroscopy (AAS) was used to calculate removal efficiency. These optimized results were compared with As(III) removal experiments conducted with different nature of water sample using crosslinked TPVA. In order to study the effect of competitive ions, the removal studies were carried out in the presence of salts solutions of various ions at different concentration. Results obtained revealed that the crosslinked TPVA behave as a good chelating material for As(III). A removal efficiency of approximately 94.5% was obtained.

In order to determine the reusability of the crosslinked TPVA the removal and regeneration process was repeated several times. The arsenite riched crosslinked TPVA membrane has been used for the regeneration process at different conditions, after different cycle efficiency of crosslinked TPVA has a slightly less. However, it may be possible to regenerate the chelating material by various treatments. The present investigation focuses on the development of good antifouling crosslinked TPVA-based arsenite chelating material. The resulting material has excellent anti fungal properties because of the ionic crosslinker STMP (good antifouling agent). The antifungal studies of different TPVA material have been carried out by colony count method against a standard strain of *Candida Albicans (*ATCC 90028). The material has shown good regeneration ability with antifungal property.

As we know that arsenic is a natural metalloid and found in the atmosphere, soils and rocks, natural waters and organism permanently. It cannot be completely removed from the environment only can be transformed from one form to another from. The inorganic forms consisting mostly of arsenite and arsenate compounds are toxic to human health. But the various available literatures indicate the wide application of arsenic in extensive routes for human survival like medicines, agriculture and industries. Therefore, arsenic collected through the separation and regeneration process can be put to use in the areas where its usage is most valued at very low concentration. As we know that PVA is complete biodegradable polymer while other components also used in this study are non toxic and biodegradable, the TG-FTIR data support this statement after decomposition there is no toxic components release into the environment. Due to this manner taking into account the newly functionalized TPVA is the suitable solution of regeneration and disposal waste management streams.

The arsenic removal efficiency is reported 95%, while for the complete separation of arsenic ions from water to safe levels the sequencing of the material has been used. The remaining studies i.e. total dissolve solid, conductivity and various other parameters regarding the swelling and the removal efficiency of polymer will observe in the commercialization process. These are the few future perspective of this works.