SYNTHESIS OF BIODEGRADABLE METAL ADSORBENT BY GRAFT POLYMERIZATION ONTO COTTON FOR THE REMOVAL OF HEAVY METAL FROM INDUSTRIAL EFFLUENT

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A thesis submitted in partial fulfilment of the requirements for the degree of
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CERTIFICATION

The thesis titled "SYNTHESIS OF BIODEGRADABLE METAL ADSORBENT BY GRAFT POLYMERIZATION ONTO COTTON FOR THE REMOVAL OF HEAVY METAL FROM INDUSTRIAL EFFLUENT" submitted by **Md. Sabur Ahammad Khan** (Student ID: **17MCHEM014P** of Session: 2017-18) has been accepted as satisfactory in partial fulfillment of the requirement for the degree of **Master of Philosophy in Chemistry** on 11 July,2024.

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Dedication

To my beloved parents, infinitely supportive

Conference

Conference

- 1st International Symposium on Materials, Energy and Environment (ISMEE24), 03 May 2024, Department of Chemistry, University of Chittagong.

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This is to certify that Md. Sabur Ahammad Khan has carried out this research work under my supervision, and he has fulfilled the requirements of the relevant Academic Ordinance of the Chittagong University of Engineering and Technology so that he is qualified to submit the following Thesis in the application for the degree of Master of Philosophy in Chemistry. Furthermore, the Thesis complies with the PLAGIARISM and ACADEMIC INTEGRITY regulations of CUET.

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Abstract

Heavy metal containing industrial effluents represent a substantial hazard to the environment and human health. Heavy metal removal from wastewater is critical for mitigating its negative consequences. In this study, two noble biodegradable adsorbents were synthesized for the removal of heavy metals from contaminated water. The first absorbent poly(triethylamine methacrylate) (Cotton-*g*-PTEAMA) was prepared by grafting triethylamine (TEA) onto Cotton grafted poly(glycidyl methacrylate) (cotton-*g*-PGMA) to remove heavy metals namely Fe and Cr from industrial effluent. The successful synthesis of Cotton-*g*-PTEAMA was confirmed by Fourier-transform infrared spectroscopy (FTIR). The adsorption behaviour of Cotton-*g*-PTEAMA towards Fe and Cr from contaminated water were studied at different pH, times, and metal concentrations. The obtained data were fitted to different models of adsorption kinetics and adsorption isotherms. The adsorption rate of metals showed good fitting to the pseudo-first-order kinetic model for both Fe and Cr, and the adsorption reached equilibrium within 150 min. The isotherm studies indicated that the obtained data showed good fitting to the Freundlich model for Fe and Langmuir model for Cr. The maximum adsorption capacities of Fe and Cr for cotton-*g*-PTEAMA were found as 12.68, and 34.72 mg g–1, respectively. The second adsorbent cotton *grafted* poly(ethylenediamine methacrylate) (Cotton-*g*-PEDAMA) for the removal of heavy metals from wastewater was developed through functionalization of ethylene diamine (EDA) onto cotton-*g*-PGMA . The adsorption behaviour of cotton-*g*-PEDAMA towards Fe and Cr from contaminated water were also studied at different pH, times, and metal concentrations. The results showed that cotton-*g*-PEDAMA has an outstanding adsorption capability for Fe and Cr ions from contaminated water. The adsorption rate of metals showed good fitting to the pseudo-first-order kinetic model for both Fe and Cr, and the adsorption reached equilibrium within 120 min. The isotherm studies indicated that the obtained data showed good fitting to the Freundlich model for Fe and Langmuir model for Cr. The maximum adsorption capacities of Fe and Cr for cotton-g-PEDAMA were 44.27, and 174.4 mg g–1, respectively. Regeneration experiments indicated that the adsorbent maintained above 80% efficiency even after five adsorption/desorption cycles for both cotton-g-PTEAMA and cotton-g-PEDAMA. The adsorbent was effectively utilized to remove Fe and Cr from samples of industrial effluent. In comparison to existing treatment approaches, which frequently use non-biodegradable materials or expensive technology, the studied method shows potential as an eco-friendly option for heavy metal removal. By utilizing biodegradable materials, this study may contributes to resolve environmental problems connected with heavy metal pollution in industrial effluents. The findings may have consequences for long-term wastewater treatment practices, encouraging healthier water resources, and protecting human health.

বিমূর্ত

শিল্প বর্জ্য ধারণকারী ভারী ধাতু পরিবেশ এবং মানব স্বাস্থ্যের জন্য একটি উল্লেখযোগ্য বিপদ প্রতিনিধিত্ব করে। বর্জ্য জল থেকে ভারী ধাতু অপসারণ এর নেতিবাচক পরিণতি প্রশমিত করার জন্য গুরুত্বপূর্ণ। এই গবেষণায়, দূষিত জল থেকে ভারী ধাতু অপসারণের জন্য দুটি মহৎ বায়োডিগ্রেডেবল শোষণকারী সংশ্লেষিত হয়েছিল। প্রথম শোষক পলি (ট্রাইথাইলামাইন মেথাক্রাইলেট) (Cotton-g-PTEAMA) তুলা গ্রাফটেড পলি (গ্লাইসিডিল মেথাক্রাইলেট) (তুলা-জি-পিজিএমএ) এর উপর ট্রাইথাইলামাইন (TEA) গ্রাফট করে তৈরি করা হয়েছিল যাতে শিল্পের বর্জ্য থেকে Fe এবং Cr নামক ভারী ধাতু অপসারণ করা হয়। Cotton-g-PTEAMA এর সফল সংশ্লেষণ ফুরিয়ার-ট্রান্সফর্ম ইনফ্রারেড স্পেকট্রোস্কোপি (FTIR) দ্বারা নিশ্চিত করা হয়েছে। দূষিত জল থেকে Fe এবং Cr-এর প্রতি Cotton-g-PTEAMA -এর শোষণ আচরণ বিভিন্ন pH, সময় এবং ধাতব ঘনত্বে অধ্যয়ন করা হয়েছিল। প্রাপ্ত ডেটা শোষণ গতিবিদ্যা এবং শোষণ আইসোথার্মের বিভিন্ন মডেলে লাগানো হয়েছিল। ধাতুগুলির শোষণের হার Fe এবং Cr উভয়ের জন্য ছদ্ম-প্রথম-অর্ডার গতিগত মডেলের সাথে ভাল ফিটিং দেখায় এবং শোষণ 150 মিনিটের মধ্যে ভারসাম্যে পৌঁছেছিল। আইসোথার্ম স্টাডিগুলি ইঙ্গিত করেছে যে প্রাপ্ত ডেটা ফে-এর জন্য ফ্রুন্ডলিচ মডেল এবং Cr-এর জন্য ল্যাংমুইর মডেলের জন্য ভাল ফিটিং দেখিয়েছে। Cotton-g-PTEAMA-এর জন্য Fe এবং Cr-এর সর্বাধিক শোষণ ক্ষমতা যথাক্রমে 12.68, এবং 34.72 mg g-1 হিসাবে পাওয়া গেছে। বর্জ্য জল থেকে ভারী ধাতু অপসারণের জন্য দ্বিতীয় শোষণকারী তুলো গ্রাফ্টেড পলি (ইথিলেনডিয়ামাইন মেথাক্রাইলেট) (Cotton-g-PEDAMA) Cotton-g-PEDAMA তে ইথিলিন ডায়ামিন (EDA) এর কার্যকরীকরণের মাধ্যমে তৈরি করা হয়েছিল। দূষিত জল থেকে Fe এবং Cr-এর প্রতি তুলা-g-PEDAMA-এর শোষণ আচরণও বিভিন্ন pH, সময় এবং ধাতব ঘনত্বে অধ্যয়ন করা হয়েছিল। ফলাফলগুলি দেখায় যে তুলা-জি-পেডামা দূষিত জল থেকে ফে এবং সিআর আয়নগুলির জন্য একটি অসামান্য শোষণ ক্ষমতা রয়েছে। ধাতুগুলির শোষণের হার Fe এবং Cr উভয়ের জন্য ছদ্ম-প্রথম-অর্ডার গতিগত মডেলের সাথে ভাল ফিটিং দেখায় এবং শোষণ 120 মিনিটের মধ্যে ভারসাম্যে পৌঁছেছিল। আইসোথার্ম স্টাডিগুলি ইঙ্গিত করেছে যে প্রাপ্ত ডেটা ফে-এর জন্য ফ্রুন্ডলিচ মডেল এবং Cr-এর জন্য ল্যাংমুইর মডেলের জন্য ভাল ফিটিং দেখিয়েছে। তুলা-জি-পেডামার জন্য Fe এবং Cr-এর সর্বাধিক শোষণ ক্ষমতা যথাক্রমে 44.27, এবং 174.4 mg g–1 ছিল৷ পুনর্জন্ম পরীক্ষাগুলি নির্দেশ করে যে তুলা—জি—পিটিইএএমএ এবং কটন—জি—পেডামা উভয়ের জন্য পাঁচটি শোষণ চক্রের পরেও শোষণকারী 80% এর উপরে দক্ষতা বজায় রেখেছে৷ শিল্প বর্জ্যের নমুনা থেকে Fe এবং Cr অপসারণের জন্য শোষণকারী কার্যকরভাবে ব্যবহার করা হয়েছিল৷ বিদ্যমান চিকিত্সা পদ্ধতির তুলনায়, যা প্রায়শই নন—বায়োডিগ্রেডেবল উপকরণ বা ব্যয়বহুল প্রযুক্তি ব্যবহার করে, অধ্যয়ন করা পদ্ধতিটি ভারী ধাতু অপসারণের জন্য একটি পরিবেশ—

বান্ধব বিকল্প হিসাবে সম্ভাব্যতা দেখায়। বায়োডিগ্রেডেবল উপকরণ ব্যবহার করে, এই অধ্যয়ন শিল্প বর্জ্যের ভারী ধাতু দূষণের সাথে যুক্ত পরিবেশগত সমস্যা সমাধানে অবদান রাখতে পারে। দীর্ঘমেয়াদী বর্জ্য জল চিকিত্সা অনুশীলন, স্বাস্থ্যকর জল সংস্থানগুলিকে উত্সাহিত করা এবং মানব স্বাস্থ্য সুরক্ষার জন্য ফলাফলগুলি হতে পারে। ।

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Nomenclature

Symbols	Elaborations
e.g.	for example
etc.	Etcetera
et al	And Others
Fig.	Figure
Min	Minimum
Max	Maximum
ppm	Parts per million
λ	Wavelength
^{0}C	Degree Celsius
µS/cm	Micro Siemens/centimeter
ppt	Parts Per Thousand

Acronyms and Abbreviations

CAN	Ceric ammonium nitrate
GMA	Glycidyl methacrylate
PGMA	Polyglycidyl methacrylate
TEA	Tri-ethyl amine
EDA	Ethylene diamine
Cotton-g-PTEAMA	Cotton-grafted-polytriethylaminemethacrylate
Cotton-g-PEDAMA	Cotton-grafted-polyethylenediaminemethacrylate

Chapter 1: INTRODUCTION

1.1 GENERAL OUTLINE

Industrial activities have become an essential aspect of modern civilization, propelling economic growth and technical progress. However, these operations frequently produce enormous amounts of wastewater including hazardous chemicals, heavy metals, and other contaminants. The release of industrial effluent into bodies of water without sufficient treatment endangers both human health and the environment. In recent years, efforts have been undertaken to create effective and sustainable technologies for treating industrial wastewater (Neoh et al., 2016). Adsorption has emerged as a viable strategy among these treatments because of its high removal efficiency, adaptability, and cost-effectiveness (Chai et al., 2021). Traditional adsorbents, such as activated carbon and synthetic polymers, have undergone substantial study into their metal adsorption capability (Gupta et al., 2015).

Traditional absorbents have several drawbacks that must be addressed (Parmar & Thakur, 2013), which means they remain in the environment for an extended period of time after their Traditional adsorbents, such as activated carbon and synthetic polymers, are non-biodegradable usage. This raise worries regarding their long-term environmental effect and garbage accumulation. One of the biggest drawbacks of conventional adsorbents is their scarcity (Aghaei et al., 2017). Although commonly utilized, activated carbon is often produced from non-renewable sources such as coal or petroleum. This scarcity might result in higher costs and possibly supply chain difficulties. Traditional adsorbents frequently encounter regeneration and reusability difficulties (Baskar et al., 2022). Regenerating activated carbon is a highly complicated and energy-intensive process that necessitates high temperatures or chemical treatments. Synthetic polymers may also have limits in terms of regeneration and may deteriorate over time, limiting their usefulness (Andrady, 1994). However, their non-biodegradability and restricted availability raise worries about their long-term environmental effect. Manufacturing operations may include the usage of chemicals, energy-intensive procedures, and the development of waste byproducts. To address these challenges, the synthesis of biodegradable metal adsorbents utilizing natural materials has received a lot of interest.

Environmentally friendly biodegradable metal adsorbents are made via grafting polymerization onto cotton (Du et al., 2020). They decay naturally over time, limiting the long-term environmental effect and possible trash accumulation. Cotton is a renewable resource that is utilized as the substrate for graft polymerization (Carlmark et al., 2012). It is plentiful and can be sourced responsibly, alleviating worries about restricted availability and potential supply chain challenges. Cotton stands out as a particularly viable alternative among natural materials due to its availability, low cost, renewability, and large surface area. When compared to standard adsorbents, biodegradable metal adsorbents synthesized on cotton fibers can offer enhanced regeneration and reusability. The grafting process allows for the immobilization of functional groups onto the cotton fibers, enhancing their metal adsorption capacity and facilitating easier regeneration. The synthesis of biodegradable metal adsorbents on cotton can be a more environmentally friendly process compared to the production of traditional adsorbents. It utilizes natural materials and avoids the use of non-renewable resources and potentially harmful chemicals.

In this regard, studies have focused on the production of biodegradable metal adsorbents as a viable approach. These materials have various benefits over traditional adsorbents, including their eco-friendliness and capacity to decompose after usage, hence reducing waste formation. Cotton stands out among biodegradable materials due to its availability, inexpensive cost, and great adsorption capabilities.

We intend to study the graft polymerization of a biodegradable metal adsorbent onto cotton for the treatment of industrial wastewater. Cotton fibers have been modified with functional groups that improve their metal adsorption ability using the graft polymerization process. It is feasible to tune the characteristics of the resultant adsorbent for specific heavy metal removal applications by optimizing different parameters such as monomer content, reaction duration, and temperature. Characterization of the synthesized biodegradable metal adsorbent employing methods such as Fourier-transform infrared spectroscopy (FTIR). The material's adsorption ability will be investigated in batch studies utilizing various quantities of heavy metal ions usually seen in industrial effluents.

In this work, we provide a unique method for grafting biodegradable metal adsorbents onto cotton for the treatment of industrial wastewater. Graft polymerization allows functional groups to be immobilized onto cotton fibers, increasing their metal adsorption capability. Furthermore, the use of biodegradable polymers assures that the adsorption process and subsequent disposal have a low environmental effect.

The findings from the study have the potential to revolutionize industrial wastewater treatment by delivering a sustainable and environmentally beneficial alternative. Furthermore, the development of biodegradable metal adsorbents can help to reduce hazardous waste and encourage a more environmentally friendly approach to industrial operations. This research intends to contribute to the preservation and repair of our fragile ecosystems by tackling the environmental concerns connected with industrial wastewater.

Significant volumes of effluent-containing contaminants are produced by industrial operations, posing health and environmental dangers. Adsorption, particularly employing classic adsorbents such as activated carbon and synthetic polymers, has been widely explored for the treatment of industrial wastewater. While these classic adsorbents have advantages in terms of removal efficiency and adaptability, they also have drawbacks such as restricted availability, regeneration issues, and possible environmental concerns. To circumvent these constraints, the synthesis of biodegradable metal adsorbents on cotton fibers has emerged as a sustainable and economical solution for the treatment of industrial wastewater.

1.2 BACKGROUND OF THE PRESENT STUDY

Water contamination with toxic metals such as mercury and lead causes serious human health problems in Bangladesh. Many kinds of metal adsorbents including activated carbon, bentonite, and synthetic polymers have been developed to remove toxic metals from streaming water (McCullough & Matyjaszewski, 2010). Most of these metal adsorbents are composed of spherical resin that is synthesized by the copolymerization of styrene and divinylbenzene (Jenkins & Hudson, 2001).

These superior characteristics depend on the high diffusion rate of metal ions in the fibrous adsorbent, in which the fiber diameters of 10–20μm are ten times smaller than those of spherical resin adsorbents. Synthetic trunk polymers are, however, derived from petroleum resources. If a naturally occurring polymer such as cellulose could be used as the trunk polymer for graft polymerization, the dependence on petroleum resources in adsorbent production would decrease. Indeed, grafting on cellulose has been extensively investigated. In mutual grafting, the trunk polymer is irradiated in a monomer solution and it is necessary to suppress the formation of homo polymer (Badawy et al., 2001).

Fibrous adsorbents can be easily synthesized by radiation-induced graft polymerization. In the present study, two kinds of amine-type adsorbents will be synthesized by a novel pre-irradiation graft polymerization of emulsified glycidyl methacrylate (GMA) onto a nonwoven cotton fabric and subsequent chemical modification. The batch and continuous adsorption of mercury ions will be investigated for the modified fibrous adsorbents.

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1.3 OBJECTIVES OF THIS PRESENT STUDY

The following are the study's objectives:

- To synthesize biodegradable metal adsorbent optimizes the grafting conditions to achieve maximum metal adsorption capacity.
- To evaluate the performance of the synthesized biodegradable metal adsorbent from aqueous solutions of heavy metals in terms of metal removal efficiency, regeneration capability, and reusability.
- To assess the capability of synthesized biodegradable metal adsorbent for the treatment of industrial effluent containing heavy metals

1.4 EXPECTED RESULTS

The successful completion of this research will enhance the present level of knowledge in this field. It is expected that we can synthesize biodegradable metal adsorbent by graft polymerization onto cotton for the Treatment of industrial Effluent. This research will help to save the environment from pollution by heavy metals. From this project academic degree is expected to be awarded and good papers are also expected to be published.

Chapter 2: LITERATURE REVIEW

2.1 REVIEW ON PURE COTTON

Synthesis of biodegradable metal adsorbent by graft polymerization onto pure cotton. Here pure cotton is the media for grafting process. The properties of pure cotton are as follows:

Table 2.1. Properties of Cotton

Technical Properties	Values
Fiber density	1.52 g/cm^3
Fiber Diameter	Micronaire- 2.0-7.0 Approximate denier- 0.7-2.5
Elasticity recovery	At 2 % Extension -74% At 5 % Extension -45%
Breaking elongation (dry)	3-9.5
Tensile Strength (g per tex/g per denier)	Dry -27 – 44 / 3.0 – 4.9
	Wet -28 – 57 / 3.3 – 6.4
Moisture Regain at Standard Conditions	7%
Water Absorbing Capacity	Less than 24 grams of water per gram of fiber
Density	1.54 g/cm^3
Degree of Polymerization	9000-15000
Crystallinity by X-ray Diffraction	73%(average)
Color (Whiteness Index)	90-100

Figure 2.1 Pure Cotton

The properties of cotton outlined in Table 3.2 provide valuable insights into its suitability as a substrate for synthesizing a biodegradable metal adsorbent through graft polymerization, particularly for the treatment of industrial effluent. The moderate fibre density and diverse fibre diameter suggest potential for a material with favourable mass and surface characteristics (Yu et al., 2022). The elasticity recovery at 2% (-74%) and 5% (-45%) extension, along with breaking elongation indicate flexibility and strength critical for grafting without compromising structural integrity. Tensile strength in both dry and wet conditions (is crucial for the adsorbent's durability during water treatment processes. The moisture regains at standard conditions and water-absorbing capacity emphasize the material's interaction with aqueous environments. The density (and degree of polymerization contribute to the overall mass, volume, and structure of the adsorbent, impacting its efficiency. The crystallinity by X-ray diffraction and colour further underscore aspects of structural stability and visual appeal (Humayoun et al., 2023). In summary, these properties collectively suggest that cotton, with its diverse characteristics, holds promise as a viable substrate for creating an effective and environmentally friendly metal adsorbent for industrial effluent treatment through graft polymerization.

2.2 REVIEW ON POLYMERS

Important industrial commodities are based on polymers. In addition to social concerns, the need to replace traditional materials is the reason for their rapid increase in production. The Swedish chemist J. J. Berzelius coined the term "polymer." For instance, he thought of benzene (C6H6) as an ethyne (C2H2) polymer. This definition later had a minor alteration (Nicholson, 1991). Polymer science is a relatively recent field of study that deals with materials that are widely used in modern life, such as plastics, rubbers, coatings, adhesives, sealants, and natural and synthetic fibres.

One of the most influential concepts of the 20th century is the idea of polymers. It was first proposed in the 1920s amidst protracted debate, and the 1953 Nobel Prize winner H. Staudinger is strongly linked to its adoption. One could list a plethora of instances of synthetic polymers, some commonplace like nylon or polyester, some less well-known as the ones used for organ transplants, biodegradable sutures, etc.

Commodity plastics, which are low-cost and high-volume, and engineering plastics, which are high-volume and low-cost, can be separated based on economic and application factors. Polycarbonate (PC), poly (etherketone) (PEEK), polyimide (PI), and other materials are included in the second group, whilst polyethylene (PE), polypropylene (PP), and poly (vinyl chloride) (PVC) are considered in the first. High aspect ratios, high strengths, high moduli, and other qualities, depending on their intended uses, are characteristics of natural, synthetic, and artificial (modified natural) fibres. Rapid retraction and stretching are characteristics of elastomers.

Plastics

Parkes and Hyatt discovered the first plastic substance in 1862 and 1866, respectively, and it was based on nitrocellulose. The first thermoplastic, or modified natural polymer, known as celluloid, was created when camphor was added to nitrocellulose. By 1900, motion picture film was made using this substance.

In Germany, casein, a milk protein, and formaldehyde were reacted to create galalith (gala = milk, lithos = stone) in 1897 (Elias, 2003). Other polycondensation products based on formaldehyde (F) with urea (U) and melamine (M), referred to as amino resins, aminoplasts, or aminoplastics, were developed as a result of the successful use of PF resin. Tollens originally characterized these polymers in 1884, and John received a patent for them in 1918 (Seymour, 2012). Unlike phenoplasts, aminoplasts can be made transparent or have light hues. Rossiter created aminoplasts in 1926 using formaldehyde and a urea-thiourea combination (Russell, 2000). Midway in the 1930s, MF resin manufacture got underway.

Fibers

A fiber's thread-like structure, independent of its chemical makeup, is what distinguishes it from other materials. Mineral, biological, or metallic fibers are possible. The majority of nonmetallic fibers are composed of polymeric materials, which might be synthetic, artificial, or modified natural. Aspect ratios of 103 or higher are found in natural fabrics like cotton and wool. Whereas macromolecular silicates, which are found in glass and asbestos, are the main mineral fibers, carbon and heterochain polymers make up organic fibers. Few organic synthetic fibers are thermosets, while the majority are thermoplastic and some are elastomeric. They have less than 75 years of history (Elias, 2003).

Elastomers

Rubber trees are first mentioned in Pietro Martire d'Anghiera's De Orbe Nuovo, which was published in Latin in 1516. The magnificent natural resource, the Heveea Brasiliensis forest tree, is found in the southern equatorial region, primarily in Malaysia, Indonesia, Thailand, Ceylon, India, Cambodia, Vietnam, Brazil, Africa, and a few other Asian and South American nations. In South America, these trees were known as "Cau-uchu," or "weeping wood." The term "rub off pencil marks" refers to the material's use as an eraser, which was first described by Priestley in 1770. In many languages other than English, where it refers exclusively to the rubber hydrocarbon, the term caoutchouc, as originally used, is still used to refer to rubber.

2.3 REVIEW ON POLYMER GRAFTING

Despite its inception in the mid-1900s, the polymer system has found multiple uses to this day, making it a constant topic of interest for applied chemists(Abourehab et al., 2022; Rehman et al., 2022). The polymer sector is expanding in step with population expansion, but it is constrained by the growing demand for natural products, which is difficult to satisfy given the scarcity of supply. A novel promise based on polymer segment branches covalently attached to primary polymer chains was discovered by the grafting of polymer/copolymers (Ajaz et al., 2022; Awad et al., 2021).

Various chemical structures or homo- or copolymer combinations can make up the core and branches(Vega-Hernández et al., 2021). Synthetic chemists started to show interest in the 1980s in the prospect of producing novel conducting polymers with improved and desired properties(Khedr, 2022).

Through grafting or copolymerization with another polymer, a polymer's physicochemical properties can be further altered. Grafting polymers are very important because they attempt to introduce and assimilate the properties of the grafted materials while maintaining the extended conjugated structure in the primary chain. Grafting may be able to improve and compensate for conductivity characteristics of polymers that are not connected to charge transfer; instead, these characteristics may be related to solubility, nano-dimensional morphology, biocompatibility, bio-communication, and so forth(Heeger, 2001). In instance, conducting polymers need various additional variables in addition to electron delocalization to meet the requirements for scientific or other benefits, making them suitable for use in biomedical-based applications or technologies. Finding alternatives to this question thus far has proven to be challenging(Bhattacharyya & Maldas, 1984; McCullough & Matyjaszewski, 2010).

Graft copolymers can be made using three general techniques: The terms "grafting to," "grafting from," and "grafting through" are also condensed and more clearly depicted in Figure_ (Liu, 2018). To summarize, the process of "grafting to" involves joining pre-polymerized chains to reactive end-group backbone polymers. The approach for differentiating polymer grafting was implemented to modify the polymers in accordance with the figure shown below (Figure 1). Grafting to, pre-polymerized chains are attached to reactive backbone polymers(Zdyrko & Luzinov, 2011); Grafting from, a conducting polymer backbone synthesized with initiation side functions as a macroinitiator from where side chains are grown and Grafting through, after polymerization macromonomers are synthesized to form backbone polymers.

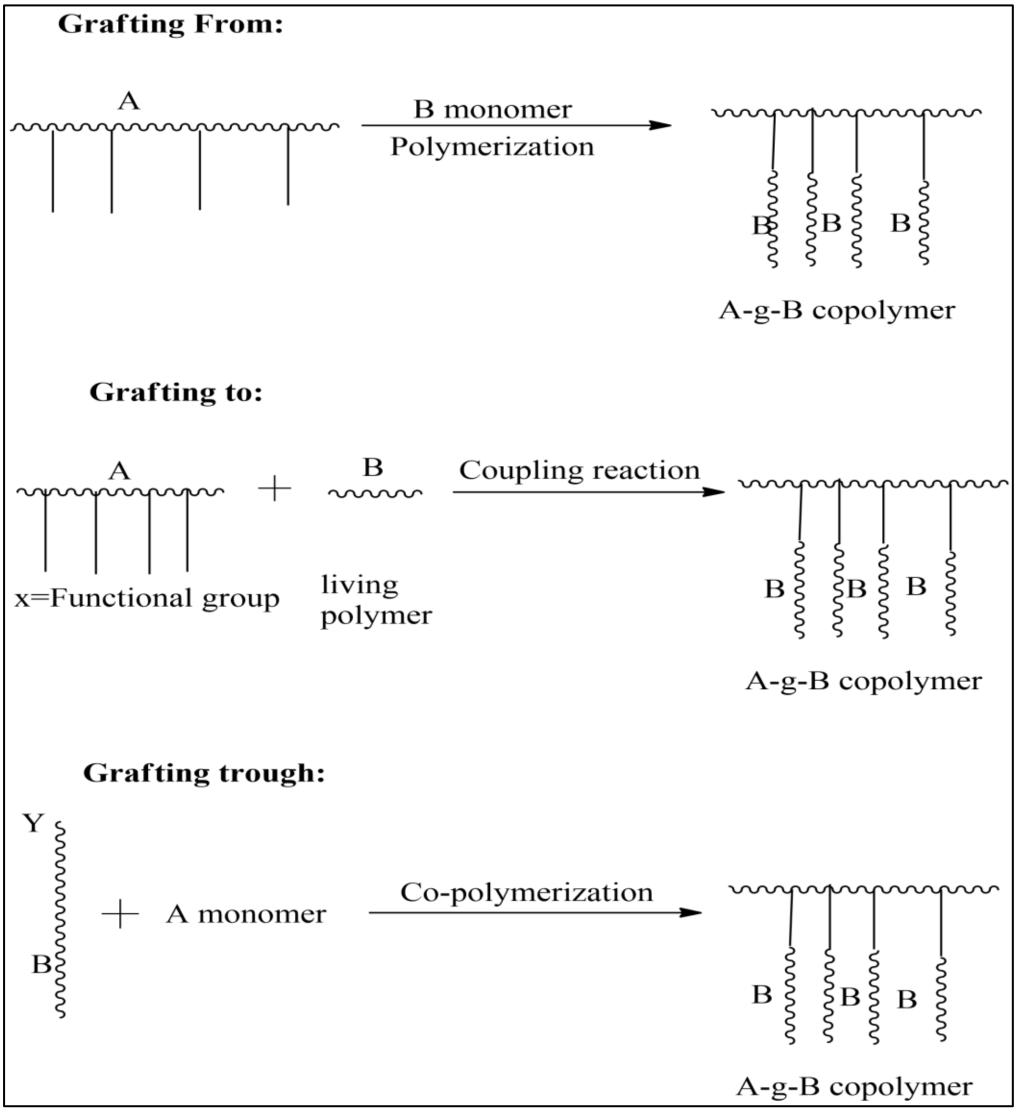


Figure 2.2 Various types of polymer grafting

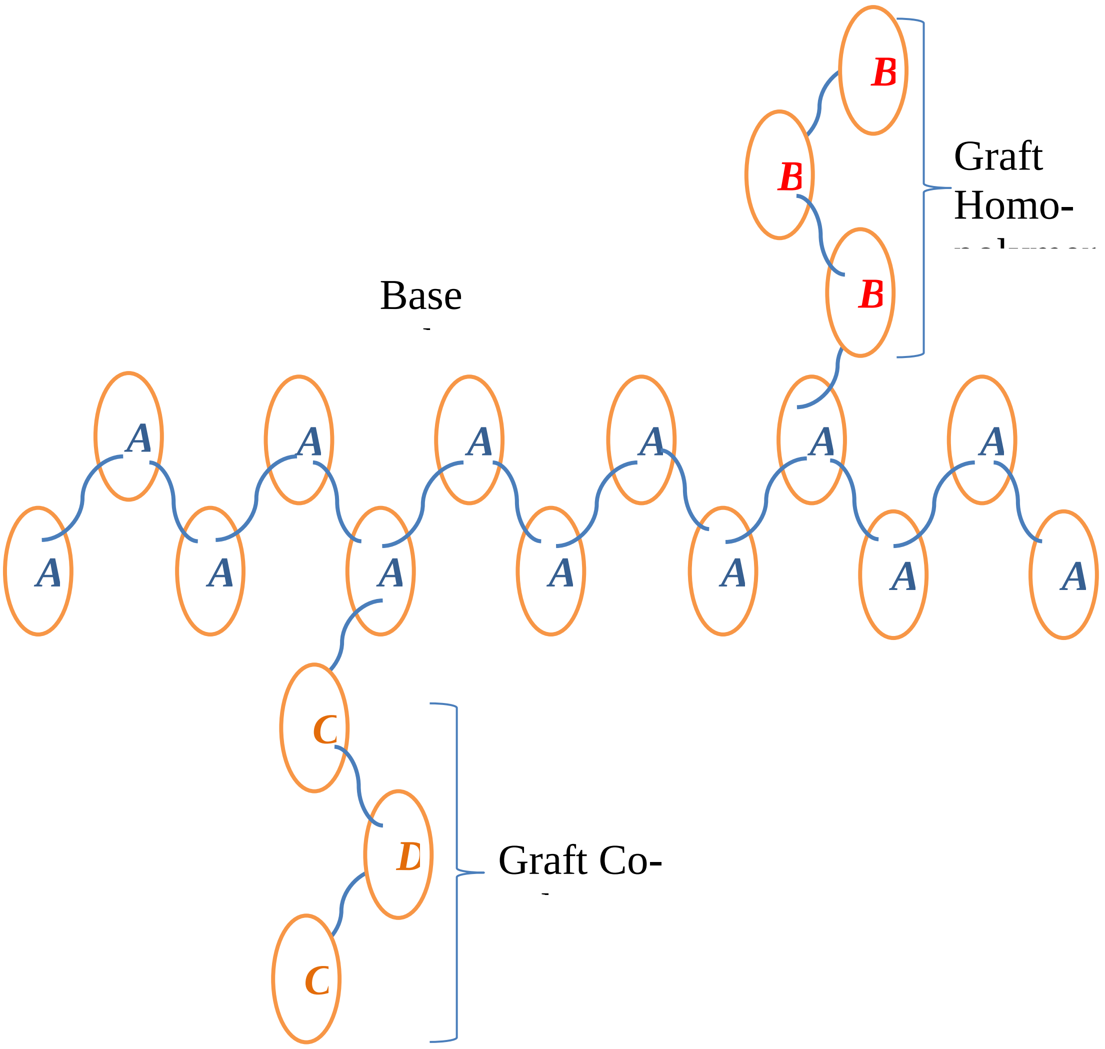


Figure 2.3 Structure of different graft polymer

2.4 METHODS OF POLYMER GRAFTING

Surface of polymers modifies or graft to improve various physical and chemical properties of polymer chain such as mechanical characteristics, biocompatibility, wettability and so on. There are basically two types of grafting:

1. Grafting with single monomer
2. Grafting with a mixture of two or more monomers

Modification of polymer chain is required to improve or provide special properties to modified materials such as their flexibility and rigidity, compatibility, physical responses, and thermal stability. Also, through modification solubility of polymer chain also changes as they can soluble and also improves the conditions for polymer processing. There are many methods for polymer modification but among them grafting, cross linking, blending and composite formation are the most common methods (Bahulkar et al., 2015)

Through coupling reaction side chains are connected to a linear backbone in the graft- to approach while the graft-from approach creates side chains from backbone initiating groups from a macroinitiator. And in the graft-through process macro monomers are polymerized which contains side chains.

Grafting is also classified as types of monomers attached as, 1. Grafting (single monomer): takes place with single step and 2. Grafting (mixture of two or more monomers): occurs when monomers are used sequentially.

An attractive method for adding a variety of functional groups to a polymer is grafted co-polymerization. Grafted polymers have an almost endless potential and a bright future ahead of them. In polymer grafting, the link between structure and properties has been a major area of study. Research on the grafting of these types of materials to create enhanced materials with significant biopolymer content (often as backbones) has been rekindled by the renewed focus on bio-based monomers and biopolymers as a practical solution to lowering (synthetic) polymer waste and disposal issues. In the current situation, the grafting polymer plays a crucial role in the multidimensional usage of cellulose, chitosan, and polysaccharides(Jenkins & Hudson, 2001; Kaur & Gupta, 2017; Slagman et al., 2018; Thakur et al., 2014).

Table 2.2. Various kinds of grafted polymers

Main polymer chain	**Grafting method**	**Graft chains**	**References**
High-density polyethylene (HDPE)	Melt free-radical grafting	GMA	(Saeb et al., 2017)
Starch	CTP (chain transfer to polymer) by free-radical polymerization (FRP)	Polyacrylamide	(Cao et al., 2003)
Poly (propylene glycol)	CTP (chain transfer to polymer) by free-radical polymerization (FRP)	Poly (styrene-co-acrylonitrile)	(Li et al., 2012)
Polyethylene	CTP (chain transfer to polymer) by free-radical polymerization (FRP)	Vinyl polymers	(Hernández-Ortiz et al., 2019)
Natural rubber latex (core-shell particles)	CTP (chain transfer to polymer) by free-radical polymerization (FRP)	PMMA	(Sirirat et al., 2015)
Polyethylene	CTP (chain transfer to polymer) by free-radical polymerization (FRP) in tubular reactor	Vinyl polymers	(Hernández-Ortiz et al., 2019)
Various surfaces	Surface initiated controlled radical polymerization	Polymers from 2-methacryloyloxythyl phosphorylcholine (MPC), methyl acrylate, acrylamide, and N-isopropyl acrylamide	(Zhou et al., 2012)

2.5 REVIEW ON TECHNIQUE OF POLYMER GRAFTING

There are some crucial factors e.g. chemical nature of components (such as monomer, solvent, initiator and backbone) and their relations can influence the polymerization techniques. Along with these there are also some terms to be considered temperature and additive use (Sosnik et al., 2011). in the figure synthetic routes of grafting techniques are represented with the activators include a variety and versatile polymer modification routes.

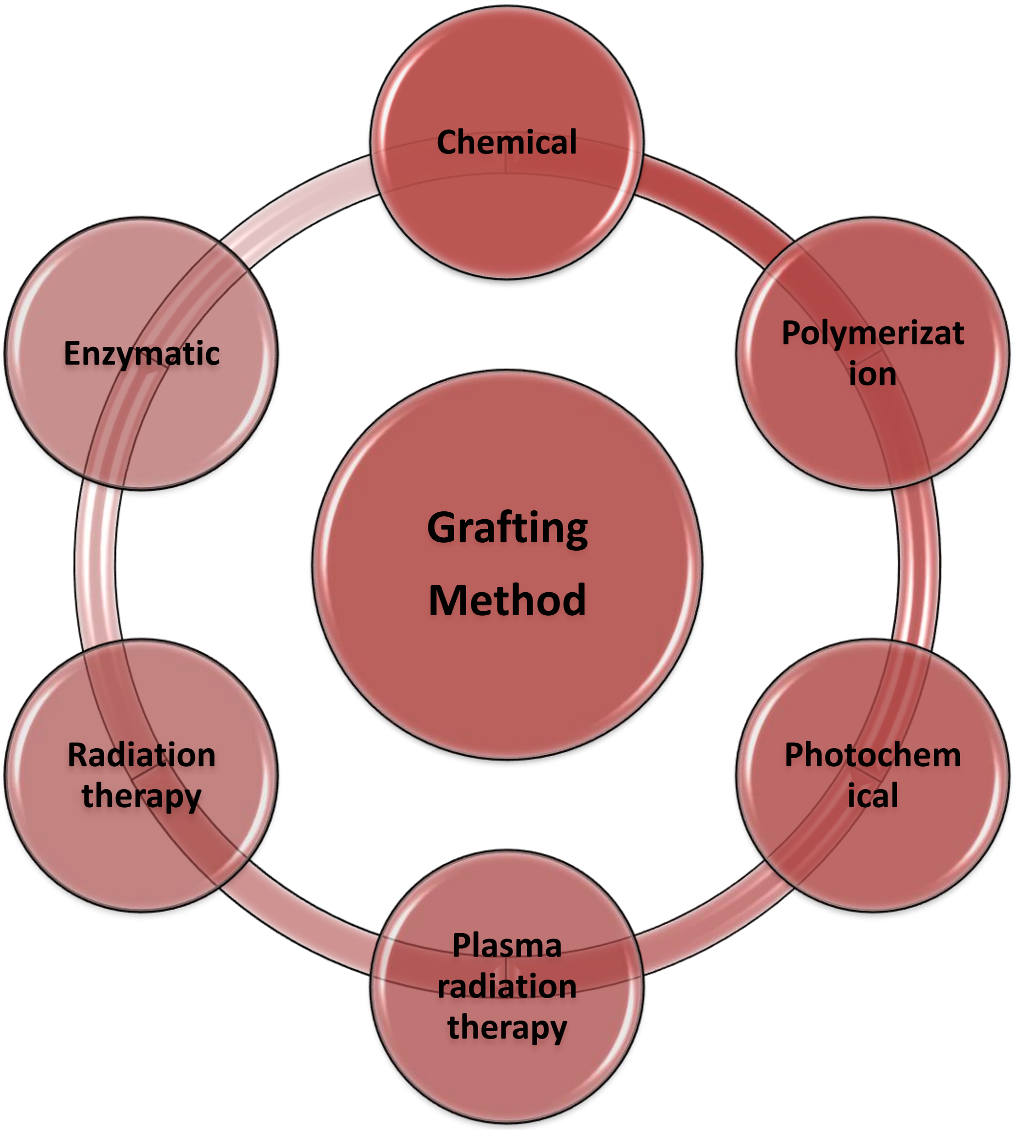


Figure 2.4 Different types of grafting metho

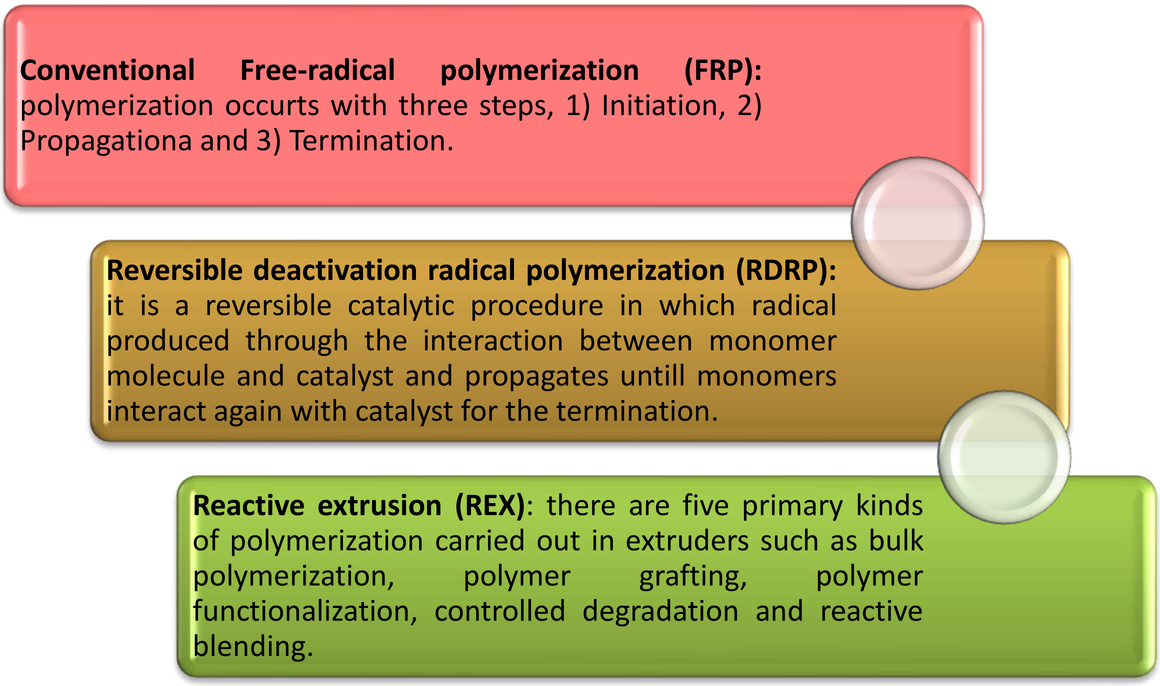
Chemical approach of grafting

There are two types of grafting routes in chemical approach: ionic initiator grafting and free radical grafting. The mechanism of grafting process depends on the initiator though the function of the initiator is very complex.

Free-radical grafting

In this grafting process generation of free radical takes place and form the graft co-polymer through the reaction with monomers when transferred to the substrate. Many polymerization techniques, such as FRP, RDRP, and REX, have been employed for the polymer grafting; nevertheless, free radical processes are the most effective due to their ability to deal with different chemical groups in a flexible manner and their resistance to contaminants. Through the process of homolytic fission caused by radiation to macromolecules, the polymer can be generated in this grafting. Free radical lifespan is influenced by the behavior of the polymer backbone, a crucial component in the formation of stable graft polymers. The backbone, monomer, initiator, and solvent of the system, as well as their interactions, are chemical elements that affect polymer grafting by FRP and other reactions (Sosnik et al., 2011).

There are several ways to polymerize, however free radical approaches (such FRP, RDRP, and REX) are usually the most effective because of their adaptability to different chemical groups and impurity tolerance. Of all accessible polymers, this process still yields about 60% of them (Šebenik, 1998). In Figure _, the different approaches are grouped as follows.



Conventional Free-radical polymerization (FRP): polymerization occurs with three steps, 1) Initiation, 2) Propagationa and 3) Termination.

Reversible deactivation radical polymerization (RDRP): it is a reversible catalytic procedure in which radical produced through the interaction between monomer molecule and catalyst and propagates untill monomers interact again with catalyst for the termination.

Reactive extrusion (REX): there are five primary kinds of polymerization carried out in extruders such as bulk polymerization, polymer grafting, polymer functionalization, controlled degradation and reactive blending.

Figure 2.5 Different types of free-radical polymer grafting

Click chemistry of graft polymerization

Click chemistry is the process of forming 1,2,3-triazole by 1,3-dipolar cycloaddition of an azide and an alkyne. Because of its quick and palatable reaction, it can be easily prepared and purified, making it suitable for a wide range of applications, including novel developments. One well-known and effective technique for creating polymeric soft materials with exact architectural and functional control is click chemistry. It's fantastic that live free radical polymerization's chain-end functionality and click chemistry efficiency can be combined (Kolb & Sharpless, 2003). To alter the product yield and its acceptability as a "click" reaction in the scientific community, Sharpless and associates significantly changed the reaction conditions in 2001. Since then, click chemistries have been established and developed in polymer science to produce different types of macromolecular materials with specific properties (Zhang et al., 2018).

Graft co-polymer using click chemistry

The branches of the graft copolymers are randomly placed along a linear backbone. Popular graft copolymer creation includes regulated lengths, backbone and side chain contents, and chosen functional groups. Graft-to, graft-from, and graft-through are the three categories into which graft copolymer synthetic approaches are separated. These tactics minimize unreacted side chains and maximize grafting efficacy. The application of CuAAC in the synthesis of graft copolymers was initially studied by Matyjaszewski and associates. A number of azido-terminated polymers, including PEO-N3, PS-N3, PnBA-N3, and PS-b-PnBAN3, were used in this instance to manufacture CuAAC using PHEMA (Poly(2-hydroxyethyl methacrylate)) with alkynyl side groups. Because to the connected side chains' stearic impediment, grafting densities for PS, PnBA, and PS-b-PnBA were less than 50%. Despite this, grafting densities for less bulky PEO side chains (Gao & Matyjaszewski, 2007; You et al., 2014).

2.6 REVIEW ON OTHER GRAFTING METHODS

Bromination

Since polystyrene bromination was created by thermally heating the molecule, this method was utilized to ensure that replacement occurred preferentially in its unsaturated portion. It was assumed that there would be little to no branching while polymerizing styrene at 70°C. Technique limitation: terminating developing chains would cause cross-linking and the creation of an intractable network throughout polymerization; this can only be prevented by the radical termination approach, which requires disproportionation above all else. A classic illustration of bromination to create an unsaturated link necessary for further polymerization is seen in the image below. Styrene polymerization typically has kinetic characteristics such as reaction rate that govern chain length and branching(Carlin & Shakespeare, 1946; Jones, 1956).

Esterification

The process of esterification involves the nucleophilic alcohol reacting with the carbonyl that lacks electrons to form an ester bond in the presence of acid. The polymer gains a new property from these bonds without losing its inherent properties. It has been reported that the esterification of cellulose with nitric acid in the presence of sulfuric acid, phosphoric acid, or acetic acid forms cellulose nitrate, which has beneficial properties. Additionally, cellulose esters such as cellulose acetate, cellulose acetate propionate, and cellulose acetate butyrate have been found to be commercially valuable (Klemm et al., 1997).

Etherification

The main technique for chemically changing the structure of cellulose and cellulose-based materials is this one. Examples of commercially useful cellulose ethers are methylcellulose, carboxymethyl cellulose, and hydroxyalkyl celluloses. Reacting cellulose with bi- or poly-functional chemicals to create cross-linked or resinification products inside the cellulose matrix is another way to change the structure of the material. According to Stevens (1990) and Freire et al. (2006), these techniques can consolidate the cellulose structure and provide it crease resistance, or "durable press" qualities (Carraher Jr, 2003; Freire et al., 2006).

Chain transfer

In cellulose grafting, the chain transfer reaction is frequently employed. Nevertheless, the way the reaction ends raises some concerns; in the case of cellulose chain transfer, the polymerization is halted by removing hydrogen atoms from the cellulose molecule, which results in the formation of radicals from the cellulose backbone. Since purely radical transfer graft copolymerization does not result in higher graft yields, thiol or xanthate ester groups are introduced in a variety of situations. Substances with higher chain transfer action, such as thiol groups, can be introduced into the cellulose molecules prior to grafting. Potassium persulfate initiation results in the creation of the activating species on the enlarged cellulose substrate backbone (Chaudhuri & Hermans, 1961; Pulat & Isakoca, 2006).

Ionic and ring opening graft polymerization

Due to the strict reaction conditions required for ionic polymerizations, ring opening graft and ionic polymerization have received little attention. The cation-mediated grafting of isobutylene and alpha methyl styrene onto a cellulosic substrate was studied by Rausing and Sunner. The acrylonitrile, methacrylonitrile, and methyl methacrylate graft polymers on cellulose were produced by anionic graft polymerization (Bhattacharyya & Maldas, 1984; Perrier & Takolpuckdee, 2005).

Ring opening polymerization from cellulose fiber

Using solid cotton and paper cellulose as initiators, Hafren and Cordova reported the first direct organic acid-catalyzed ring opening polymerization of cyclic monomers such as epsilon-caprolactone (epsilon-CL). The degree of graft polymerization was measured by the ratio of free initiator to monomer (Zong et al., 2016).

2.7 REVIEW ON CEHMISTRY OF POLYMER GRAFTING

The following are the three primary chemical pathways for polymer grafting: "grafting from," "grafting onto," and the macromonomer or macromer (or "grafting through") approach. Reviews in general that concentrate on grafted copolymer synthesis are available (Roy et al., 2009; Slagman et al., 2018; Vega-Hernández et al., 2021; Wohlhauser et al., 2018). Backbone activation techniques, the varieties of backbones and grafts, There have been reviews done on particular features or subtopics linked to these concerns since the graft growing routes, characterization methodologies, quantification methods of grafting and branching molar mass distributions, and applications are so extensive. For example, reviews have been written about the following: laccase-mediated grafting onto synthetic and biopolymers(Slagman et al., 2018); radiation-induced RAFT-mediated graft copolymerization(Barsbay & Güven, 2009); grafting onto chitin/chitosan(Jenkins & Hudson, 2001; Thakur et al., 2014); grafting onto cellulose or cellulose nanocrystals(Roy et al., 2009; Wohlhauser et al., 2018); grafting onto natural polymers and biofibers(Gandhi et al., 2019; Wei & McDonald, 2016); microwave-activated grafting(Kaur & Gupta, 2017; Muñoz Prieto et al., 2012); and polymer grafting onto inorganic nanoparticles to name a few(Francis et al., 2014).

Short summaries of these chemical pathways are given here. A summary of the grafted copolymer materials synthesized between 1950 and 1970 is given in Table

1, along with a few more more recent examples. The techniques and procedures considered are backbone structure, functionalization or active site generation, grafted arm structure, polymer grafting technique, polymer grafting conditions, measured properties and characterization methods, and related references. The sections that follow in this review discuss the literature on polymer grafting onto cellulose, chitin/chitosan, lignocellulosic biopolymers, other polysaccharides and natural biopolymers, inorganic materials, and metallic surfaces.

2.7.1 Main backbones used in polymer grafting

A polymer molecule known as a "backbone" is one that holds up polymeric side chains, sometimes known as "grafts" or branches. Side chains can be added to the backbone either after the backbone has been produced or during the synthesis of the backbone (a circumstance known as copolymerization)(Chung, 2002). Polymers with homogeneous bulk characteristics are obtained in the first scenario. Since it permits the alteration of numerous polymeric components, such as inorganic and metal particles as well as natural and synthetic fibers, the second scenario is highly alluring. Backbones that have undergone polymer modification typically exhibit negligible bulk property changes. Because surface modification is frequently performed using a "grafting from" technique, surface initiated polymerization (SIP) is another name for this process(Zhou et al., 2016).

Inorganic and metal surfaces, as well as synthetic and biopolymeric backbones, can be employed in polymer grafting. Polyolefins, vinyl, fluorinated polymers, nylons, and other materials are examples of synthetic polymers, which are man-made polymers. Synthetic graft copolymers are used in biomedical applications, stimuli-responsive materials, and antifouling membrane production(Ayyavoo et al., 2016; Sun et al., 2019; Weber et al., 2012). Living creatures make biopolymers in their cells. The qualities of polysaccharides—availability, biocompatibility, cheap cost, and non-toxicity—have made them relevant in recent times as potential replacements for products derived from petroleum(Garcia-Valdez et al., 2018).

Graft copolymers based on polysaccharides are utilized in food packaging, wastewater remediation, and medication delivery. The polysaccharides cellulose, lignin, chitin/chitosan, starch, and different gums are some of the most researched ones. Since polymer coatings change the interfacial properties of the modified particles, surface functionalization of inorganic and metallic particles that enable the inclusion of polymer shells by polymer grafting has also become essential. (Zhou et al., 2012) examined the many uses of metallic and inorganic particles grafted with biopolymers and Silica is one significant inorganic surface that has been altered by polymer grafting(Radhakrishnan et al., 2006; Zhou et al., 2016).

2.7.2 Backbone functionalization method

The large range of backbones of interest has led to the development of several chemical modification techniques. The presence or lack of functional groups along the backbone affects chemical modification processes. There are two main chemical pathways that have been postulated to attach, grow, or graft polymer molecules onto lignin: (a) the functionalization of hydroxyl groups and (b) the formation of new chemically active sites(Vega-Hernández et al., 2021). A polymer's reactivity is increased when functional groups are added to its backbone, opening it up to coupling or forward polymerization processes. Therefore, in order to produce the reactive end of the macromolecule species used in the "grafting through" and "grafting to" polymer grafting procedures, or the end functional pre-formed polymer, functionalization reactions are necessary (Foster et al., 2017; Roy et al., 2009).

The functionalization reactions sulfonation, esterification, etherification, amination, phosphorylation, and thiocarbonation are among the most significant ones in polymer grafting.

2.7.3 Backbone activation method

Making use of polymer grafting activators, including free-radical initiators, is another technique to create grafting sites inside the polymer backbone. Polymer grafting activators fall into three categories, as seen in Figure_: physical, chemical, and biological.

Physical activation

Ionizing radiation, often known as high energy radiation, encompasses electron-beam and γ-beam radiations. Radiation-promoted grafting can proceed in one of three ways: (a) pre-irradiating the backbone in the presence of an inert gas to produce free radicals before the backbone comes into contact with monomers; (b) pre-irradiating the backbone in an oxygen or air-filled environment to produce hydroperoxides or di-peroxides on its surface, followed by a high-temperature reaction with monomer; and (c) using the mutual irradiation technique, in which the backbone and monomer are both irradiated simultaneously to produce free radicals(Bhattacharya, 2000).

Free radicals are produced when UV light is absorbed by the materials' surface, and these radicals act as nucleation sites. For the ensuing polymerization(Hong Anh Ngo et al., 2017), the surface is subsequently brought into contact with monomer.

By directly interacting electromagnetic radiation with polar molecules and ionic particles, microwave irradiation produces extremely quick non-contact internal heating that speeds up reactions and increases yields.

Under microwave radiation, Singh et al. successfully polymerized acrylamide on guar gum. They put up a theory explaining how microwave radiation's influence on the hydroxyl group of biopolymers generates free radicals inside the polysaccharide backbone(Singh et al., 2004).

Chemical activation

Chemical activators include backbone oxidant initiators and free radicals, as Figure 1 illustrates. Compounds that exhibit either direct or indirect homo-lytic fission are known as free radical initiators. In the first scenario, the initiator acts alone, whereas in the second, the involvement of an additional environmental molecule is necessary. Activation sites are created when oxidant initiators have a direct reaction with functional groups in the backbone. The literature contains reports of polymer grafting of polysaccharides utilizing oxidant initiators (Bhattacharya, 2000; Bhattacharyya & Maldas, 1984).

Biological activation

Under mild reaction circumstances, enzymes catalyze polymer modification reactions through functional groups at side branches, along the main chain, or at chain ends. This promotes highly selective nondestructive transformations on backbones. Recently, lignin grafting employing laccases to oxidize its phenolic structures has been found to be successful (Slagman et al., 2018).

Combined activation

It has been possible to successfully do polymer grafting using a combination of chemical and physical activators. For example, to produce hydrogels synthesized by crosslinking graft copolymerization, microwave assisted polymerization (MAP) has been combined with chemical activators. This approach takes advantage of the short reaction durations needed to achieve high yields(Kumar et al., 2017; Sosnik et al., 2011). Additionally, enzymes are utilized in conjunction with radical initiators to improve the efficiency of grafting copolymerization methodologies(Cannatelli & Ragauskas, 2016; Fan et al., 2006).

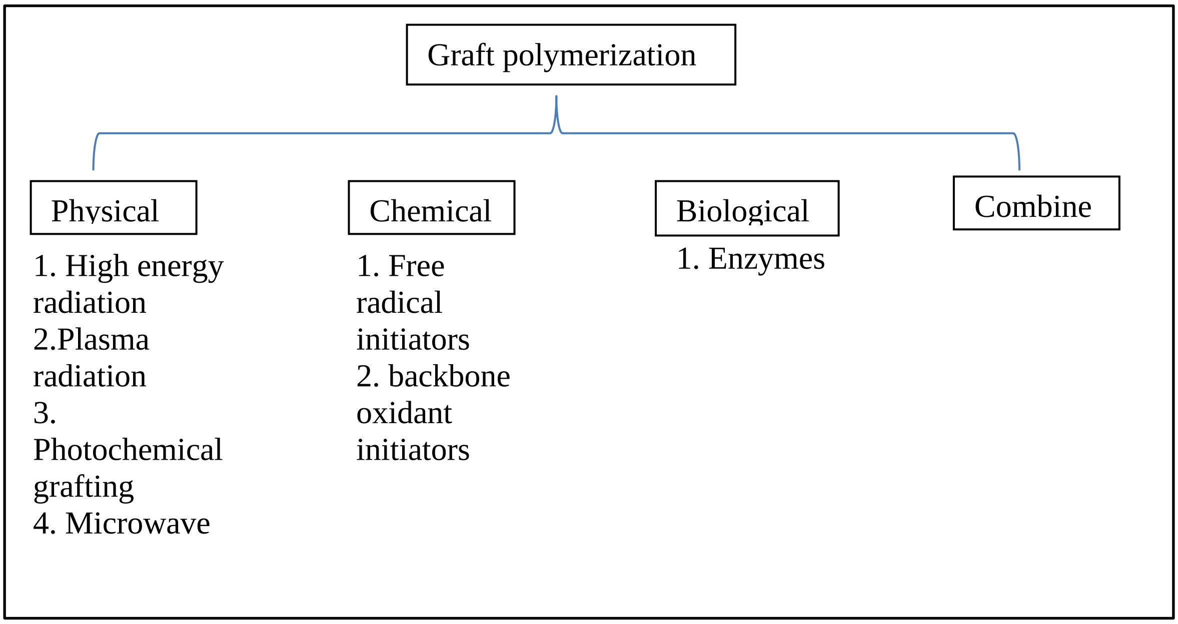


Figure 2.6 Various types of activators used in graft polymerization

2.7.4 Types of backbone used in grafting

As previously mentioned, grafted materials are made up of arms or side chains that are joined to primary polymers known as backbones. By grafting polymers together, one can combine their mechanical, chemical, electrical, interfacial, or other properties. components. In this part, a quick overview of the variety of backbones and the methods used to link side chains to them through polymer grafting will be provided.

Cellulose, lignin as backbone

In nature, lignocellulosic biopolymers are widely distributed. They consist of lignin, hemicellulose, and cellulose. In smaller quantities, they also contain moisture, extractive organic molecules, and ashes from inorganic components. Every one of these parts has unique qualities. The extractive organic substances found in lignocellulosic biopolymers include low molecular weight oligomers and oligosaccharides, sugars, fatty acids, resins, and others(Monties, 1980).

Polymer grafting is a potential technique that can be used to modify cellulose, hemicellulose, and lignin to create novel materials with intriguing features. Since the extractables are not a component of a stiff framework or skeleton that could offer support or mechanical stability, they are not helpful for this purpose. Reactants needed for the grafting procedure are also consumed by extractables. They are typically taken out before the polymer grafting procedure, albeit in certain investigations, they stay in the system while the grafted arms form .
Research on the polymer grafting of xylan onto lignin dates back to the early 1960s. Early studies on the subject described the grafting of organic polymers onto lignin or lignin derivatives, including methyl methacrylate polymers (Koshijima & Muraki, 1964; Koshijima & Muraki, 1965), xylan , ethylbenzene, and styrene (Koshijima, 1966; Koshijima & Muraki, 1966; Koshijima & Muraki, 1967;

Koshijima et al., 1968; Koshijima & Timell, 1966). Due to concerns about the environment and sustainability, the topic of polymer grafting synthetic polymers onto lignocellulosic biopolymers has become more relevant in the recent two decades (Bhattacharyya & Maldas, 1984; Feldman et al., 1986; Mansour & Nagaty, 1985; McDowall et al., 1984; Pantelakis & Tserpes, 2020; Rol et al., 2019; Slagman et al., 2018; Vega-Hernández et al., 2021).

Table 2.3. Various cellulose based grafted polymers, their properties and characterization techniques

Backbone	**Graft technique**	**Graft chains**	**Functionalization method**	**Characterization and properties**	**Refs**
Cellulose	grafting from	PSty, PAN	FRP by a KPS-FAS REDOX system.	GP, gravimetric method; FTIR and TGA to corroborate GP	(Chauhan et al., 2002)
Cellulose fabric	grafting from	PIA	FRP by KPS initiation.	GP, gravimetric method; FTIR, XRD, TGA and SEM to corroborate grafting	(Sabaa & Mokhtar, 2002)
Cotton fabric	Grafting from	PMMA, PAA, PAN, PAM	FRP by a cellulose thiocarbonate-AIBN redox system	Degree of grafting (GP), gravimetric method.	(Zahran et al., 2004)
Cellulose microfibers	Grafting through	PAA	Redox initiation.	GP, gravimetric method; FTIR and TGA to corroborate GP.	(Toledano-Thompson et al., 2005)
Cellulose powder	grafting from	N′N′-MBA , or N-VP (Gupta & Sahoo, 2000,	Co(acac)3	cellulose conversion (% CC), and total conversion (%	(Gupta & Sahoo, 2000, 2001)

		2001; Popescu et al., 2013; Popescu et al., 2012)		CT) by gravimetric methods	
Cellulose cotton fibers	grafting to	MTC-b-CD	Na2CO3 and thermal activation	FTIR and microbiological tests. Gravimetric methods and analytical modeling.	(Popescu et al., 2013; Popescu et al., 2012)
Microcrystalline cellulose	grafting from	PLLA	Ring-opening polymerization (ROP) of L-LA with DMAP in an ionic liquid	XRD, TEM, HPLC, 1HNMR, UV analysis	(Dai et al., 2014)
Cellulose nanocrystal (CNC)	grafting from	PLLA	L-LA in situ polymerization using MgH2 as redox agent	XPS, DSC, 1HNMR, 13C-NMR, FTIR, XRD, XRF, TGA and SEM	(de Paula et al., 2016)
Cellulosic filter paper	grafting from	Acrylonitrile	Radiation induced graft co-polmerization	FTIR, XRD, XRF, TGA and SEM	(Badawy et al., 2001)

2.7.5 Polymer backbone

The most popular substrates for grafting alteration are polymer backbones. Numerous combinations can be made by combining a few different strategies. The majority of these advancements are geared toward improving property for use in industrial settings. Among these are the synthesis of adhesives, the augmentation of mechanical qualities, the enhancement of chemical resistance, the synthesis of electro, optical, and thermos responsive polymers, applications in healthcare, and the creation of self-healing polymers (Iyer et al., 2015).

The early studies contain polymers based on acrylamide and acrylonitrile that were created by polymer grafting procedures. Nonetheless, during the past three decades, reversible deactivation radical polymerization (RDRP) techniques have advanced to the point where a significant amount of research has been conducted on the synthesis of materials with controllable microstructures employing polymer grafting techniques (Bednarek, 2016; Derry et al., 2016; Mocny & Klok, 2020; Wang et al., 2019; Yildirim et al., 2018). The three main RDRP pathways are atom transfer radical polymerization (ATRP) (Chmielarz et al., 2017), reversible addition fragmentation transfer polymerization (RAFT) (Derry et al., 2016; Olivier et al., 2012; Radzevicius et al., 2017), and nitroxide mediated polymerization (NMP) (Vivaldo-Lima et al., 2002). Other polymer synthesis methods that can be employed include click chemistry and ring-opening polymerization (ROP) (Bednarek, 2016). The solvent employed in the reaction is another crucial factor in polymer grafting, especially when the process is heterogeneous.

Table -2.3 provides an overview of journal publications on polymer grafting from the current period (2020–2021), giving readers an idea of the topics covered in research papers that use this chemical approach for polymer modification. As anticipated, there is a noticeable trend toward the use of synthetic polymer arms to enhance natural biopolymers.

2.8 REVIEW ON APPLICATION OF GRAFT POLYMERIZATION

Plastic industry

In most of the earlier applications, polymers have now supplanted numerous traditional methods, such as those involving metal, wood, ceramics, and glass. It was anticipated that renewable degradable plastic would be produced by mixing polymethyl methacrylate with two biodegradable initiator sources, such as starch and natural rubber latex (Dilara & Briassoulis, 2000).

Textile industry

When the grafted polymer was utilized at the ideal dosage, its flocculation efficacy was starting at pH 4.0 for the removal of suspended solids (SS) and pH 7.0 for the removal of TDS. The highest elimination of SS (94.4%) takes place over an hour of contact time at acidic pH (4.0), neutral pH (7.0), and alkaline pH (9.2), with just 10.5% and 44.3% SS excluded. The highest elimination of TDS (80.6%) was observed at pH neutral (Kumar et al., 2017).

Medicinal filed

A wide variety of grafted natural polysaccharides are used in medication delivery systems of various kinds. Pharmaceutical and biomedical companies have employed natural polysaccharides and their derivatives to control drug distribution. The main advantages of a CDDS are the preservation of an ideal concentration, frequently for extended periods of time, the enhancement of the efficacy of responsible medications due to their resistance to harsh environments, and the reduction of unwanted effects due to the high initial blood concentration (Singh et al., 2000).

Other

According to (Alves & Mano, 2008), the science of membrane separation has been impacted by polymer grafting techniques, which involve conducting polymers and hydrogels. Although chitosan is an effective flocculating material only in acidic media, the grafting polymer technique, by derivatization of substituent carboxyl groups, modulated the physicochemical property of chitosan and demonstrated zwitterionic properties such as good flocculation capabilities in both acidic and basic mediums. The grafting of PVA polymer with PLGA to increase the material's ability to transport biomolecules was demonstrated. They achieved this by attaching amine or sulfobutyl functional groups to the PVA backbone, which makes it easy to create surfaces with negatively or positively charged surface properties.

According to (Jung et al., 2001), this grafting process increased hydrophilicity, which enhanced the capacity of biomolecules to carry greater weight. Eldin et al. (2015) generated chitosan (CS) grafted alginate hydrogel by clicking chitosan strands onto NH2 groups and utilizing coupling agent P-benzoquinone (Cai et al., 2005; Omar, 2015). This technique is known as "grafting to." In order to create hydrogels from chitosan grafted with poly(N-isopropyl acrylamide) (PNIPAAm), (Cai et al., 2005)employed radiation. As the volume or proportion of grafted branches rose, the swelling behavior among these chitosan-g-PNIPAAm hydrogels improved. Chitosan that has been grafted with acrylic acid has been found to have many potential applications as a method for creating hydrophilic and bioadhesive polymers.

Natural polymer grafting

The several applications of natural based polymer grafting are compiled in Table-2.4 which is provided below. This method was the most effective means of utilizing and modifying the unique properties of natural polymers, particularly in the targeted administration of the active medication.

Table 2.4. Various natural grafted polymers

Polymer backbone (gum, natural)	Grafting technique	Application	Reference
karaya	Heat method	Treating diarrhea, gelling agent, muco and buccal adhesive	(Gandhi et al., 2019)
Xanthum gum	Thermal method and chemical modification	In the treatment of cancer, ulcerative colitis and lowering cholesterol	(Vendruscolo et al., 2005)
Acacia	Chemical modification	Dental plaque, osmotic delivery of drug	(Patel et al., 2008)
Okra	Chemical modification	Cancer treatment (lung and oral), bone strengthen, control drug delivery	(Mishra et al., 2008; Sah, 2016)
Gellan	Microwave mediated grafting	Lowering cholesterol, sustain drug delivery, thickening agent	(Deogade et al., 2012; Gandhi et al., 2019)
Gaur	Chemical modification	Film coating purpose, disintegrating agent	(Chaurasia et al., 2006; Singh et al., 2014)
Sesbania	Chemical modification	Used as gelling agent	(Stehling et al., 1998)

2.9 GRAFT POLYMERISATION FOR SUSTAINABLE HEAVY METAL REMOVAL FROM INDUSTRIAL EFFLUENTS

The synthesis of a biodegradable metal adsorbent by graft polymerization for the treatment of industrial effluent involves a unique and innovative approach to address the issue of heavy metal pollution in wastewater. This process aims to develop a sustainable solution that combines the benefits of biodegradability and metal adsorption to effectively remove heavy metals from industrial effluents. This process involves several steps, as follows:

1. Selection of a suitable biodegradable polymer
2. Grafting polymerization
3. Optimization of grafting conditions
4. Characterization and evaluation
5. Adsorption of heavy metals
6. Optimization of adsorption conditions
7. Regeneration and reusability

The first step in the synthesis process is the careful selection of a biodegradable polymer as the base material. The polymer should possess desirable properties such as biocompatibility, environmentally friendly nature, and excellent adsorption capabilities for heavy metals. Examples of commonly used biodegradable polymers include chitosan, cellulose, and starch (Badawy et al., 2001). For our analysis, we have chosen pure cotton.

Grafting polymerization is a technique used to attach polymer chains, known as graft chains, onto the polymer backbone. This step is essential as it enhances the adsorption capacity of the biodegradable polymer for heavy metals. Generally, two methods are used for grafting polymerization:

a. Radiation-induced graft polymerization (Gupta & Anjum, 2003): In this method, the biodegradable polymer is exposed to ionizing radiation, such as gamma rays or electron beams. The radiation initiates the formation of free radicals, which then react with monomers to form graft chains on the polymer backbone.

b. Chemical grafting (Zhou et al., 2019): In this method, a chemical initiator is used to initiate the grafting reaction. The initiator can be a peroxide or a redox system that generates free radicals. The monomers used in the grafting process react with these free radicals to form the graft chains.

The grafting process requires optimization to achieve the desired properties and performance of the biodegradable metal adsorbent. Factors such as the concentration of monomers, reaction temperature, reaction time, and initiator concentration need to be carefully controlled to ensure the successful grafting of the polymer chains onto the polymer backbone. Figure 1 represents the cotton fiber-based absorbents for the removal of metal ions from water.

Once the grafting process is complete, the resulting biodegradable metal adsorbent is characterized and evaluated for its properties and efficiency. Techniques such as Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and X-ray diffraction (XRD) are commonly used to analyze the functional groups, morphology, and structure of the adsorbent.

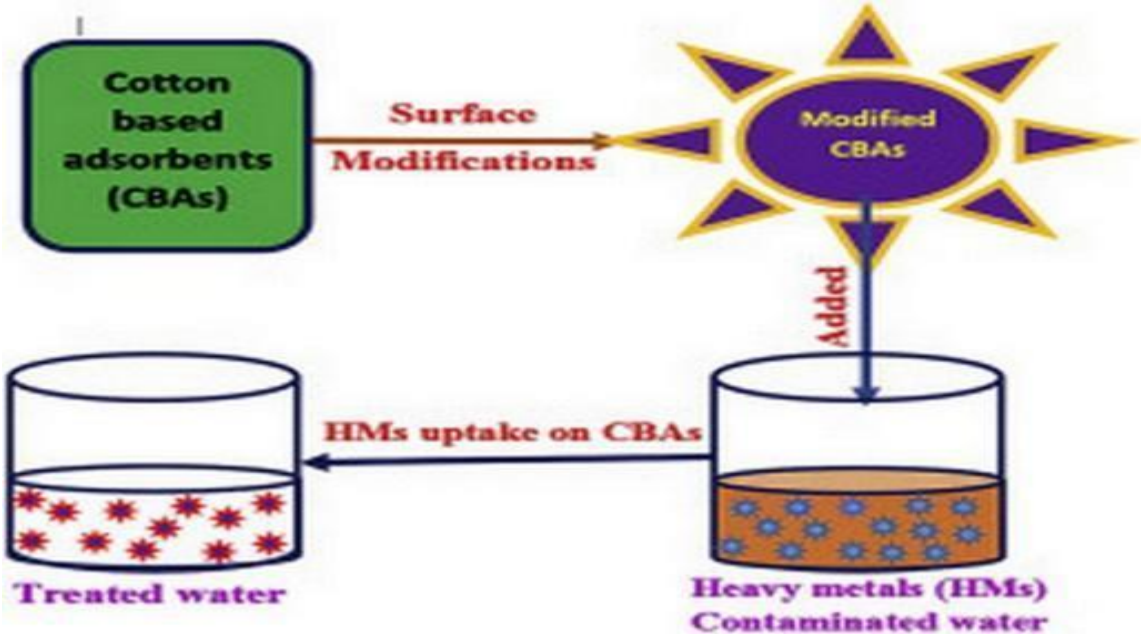


Figure 2.7 Metal ion removal from water using cotton fiber adsorbent

In the treatment of industrial effluents, biodegradable metal adsorbent is introduced into the contaminated water. The adsorption process involves the binding of heavy metal ions present in the effluent onto the surface of the adsorbent. This adsorption occurs due to the attraction between the functional groups on the adsorbent's polymer chains and the metal ions showed in figure_.

The efficiency of the adsorption process depends on various factors that need to be optimized, including the adsorbent dosage, contact time, pH, temperature, and concentration of heavy metal ions in the effluent. These parameters can be adjusted to maximize the adsorption capacity and removal efficiency of the biodegradable metal adsorbent.

After adsorption, the biodegradable metal adsorbent can be regenerated and reused. Regeneration methods such as desorption using acids, alkaline solutions, or complexing agents can be employed to release the captured heavy metal ions from the adsorbent. This process allows for the recovery of both the absorbent and the adsorbed heavy metals.

The working principle of the synthesis of biodegradable metal adsorbent by graft polymerization for the treatment of industrial effluent involves careful selection of the base polymer, grafting of polymer chains onto the polymer backbone, optimization of grafting conditions, characterization, and evaluation of the adsorbent. The adsorption of heavy metals and the optimization of adsorption conditions play a crucial role in achieving the efficient removal of heavy metal ions from industrial effluents. Additionally, the regeneration and reusability of the adsorbent contribute to the sustainability and cost-effectiveness of the overall treatment process.

2.10 PREVIOUS STUDIES ON METAL REMOVAL FROM INDUSTRIAL EFFLUENTS

In recent years, there has been a lot of interest in the graft polymerization of biodegradable metal adsorbents onto cotton for the treatment of industrial wastewater. Heavy metals included in industrial effluents constitute a major hazard to both the environment and human health. The discharge of untreated wastewater containing harmful metals can pollute water bodies, soil, and, ultimately, the food chain. As a result, effective technologies for eliminating heavy metals from industrial effluent are critical. Previous research has looked into several methods for creating biodegradable metal adsorbents by graft polymerization onto cotton. These investigations looked into a variety of topics, such as the choice of appropriate monomers, the optimization of grafting conditions, the characterization of the produced adsorbents, and their performance in metal adsorption. Some notable studies leading us to adopt Biodegradable Metal Adsorbent for the water treatment of industrial effluent are discussed below.

In presents a detailed examination of the processes and uses of ion exchange membranes produced using radiation-induced graft copolymerization (Nasef & Hegazy, 2004). It gives a clear and brief review of the many types of membranes employed in these applications, as well as a discussion of the limitations and constraints that conventional membrane fabrication procedures confront. The scientists used ionizing radiation to form an active radical in the fibrous trunk polymer, and the polymeric graft chains propagated from the active radical in the trunk polymer. Because of their grafting reactivity and high mechanical strength, synthesized polymers like polyethylene and polypropylene have been employed as trunk polymer fibers in general.

In present a detailed overview of metal ion adsorbents and their production utilizing radiation grafting and crosslinking processes (Seko et al., 2005). The authors emphasize the importance of metal ion adsorbents and their applications in a variety of sectors, including environmental remediation, wastewater treatment, and nuclear waste management. It examines the shortcomings of current adsorbent materials and offers radiation grafting and crosslinking as viable strategies for improving adsorbent performance and selectivity. They go through the monomer selection process, grafting methods, and reaction parameters that impact the synthesis process, offering a thorough grasp of the methodologies used. The study goes on to discuss the characterization methodologies used to assess the performance of the synthesized adsorbents, such as adsorption capacity, selectivity, and stability. The authors emphasize the importance of these properties in determining the effectiveness of the adsorbents for various metal ions.

investigate the structure and functioning of an antimony (III) binding polyol-ligand-containing polymer brush on a porous membrane. The authors discussed the significance of antimony (III) binding and its applications in a variety of sectors, such as water treatment and environmental cleanup (Saito et al., 2004). The authors underline the limitations of traditional approaches and present a viable solution: a polyol-ligand-containing polymer brush on a porous membrane. The authors describe the synthesis procedure as well as the characterization techniques used to investigate the structure and characteristics of a polyol-ligand-containing polymer brush. They discuss the grafting procedure, ligand selection, and reaction condition optimization to assure efficient antimony (III) ion binding. The authors offer experimental data and explain the parameters impacting binding performance, such as ligand concentration, pH, and contact duration. The results show that the polymer brush containing a polyol ligand is effective at selectively binding antimony (III) ions from aqueous solutions.

Jyo et al. [20] examine the creation and use of a phosphonic acid fiber for the selective and fast removal of lead (II) ions. The authors discuss the phosphonic acid fiber manufacturing method and offer data on the experimental settings and parameters used. They discuss how fiber shape, surface area, and functional groups contribute to excellent selectivity and quick elimination of lead (II) ions. The authors offer experimental results demonstrating the fiber's strong affinity for lead (II) ions as well as its quick adsorption kinetics. They add value to the work by discussing the elements influencing the adsorption process, such as pH, contact time, and starting lead (II) concentration, as well as focusing on the practical uses of phosphonic acid fiber in water treatment and environmental remediation. The authors contribute to the development of sustainable solutions for lead-contaminated areas by addressing the demand for effective lead (II) removal methods and proving the fiber's potential.

(Okieimen et al., 2005) present a thorough examination of the potential of cellulose graft copolymers for the removal of cadmium and copper ions from aqueous solutions. The authors clearly communicate the experimental methodologies, ensuring clarity in comprehending the copolymer synthesis and characterization. The inclusion of experimental data and graphics throughout the manuscript strengthens the credibility of the study conclusions. The authors present a full description of the findings, illustrating the adsorption capacity, isotherms, kinetics, and selectivity of the cellulose graft copolymers towards cadmium and copper ions. The study's emphasis on the practical uses of cellulose graft copolymers in dealing with heavy metal contamination adds significance to the research. By addressing the need for effective metal ion removal strategies and showing promising outcomes, the authors contribute to the development of sustainable solutions for environmental remediation.

Due to the copolymer's unique features and high sorption capacity, (Biçak et al., 1999) propose the graft copolymer of acrylamide onto cellulose as a feasible solution. The study looks into the graft copolymer's production and examines its selectivity and sorption capacity for mercury ions. The authors discuss the experimental processes in full, including the copolymer preparation and characterization techniques used. The study investigates the effect of pH, starting mercury ion concentration, contact time, and temperature on the graft copolymer's sorption effectiveness. The authors give experimental data and graphs to demonstrate sorption isotherms and kinetics, shedding light on the process of mercury ion sorption.

(Inukai et al., 2004) describe a brief but important investigation of the removal of boron (III) using an N-methylglucamine-type cellulose derivative, emphasizing its increased adsorption rate. The authors successfully demonstrate the potential of this cellulose derivative as an efficient sorbent for boron (III) removal, hence contributing to the development of viable and sustainable boron ion remediation strategies.

(Navarro et al., 2001) conducted a thorough examination of the effect of anions on heavy metal sorption utilizing a cellulose material treated with poly (glycidyl methacrylate) and polyethyleneimine. The authors deftly explain how anions influence sorption behavior, giving insight into the complicated interactions between cellulose-based sorbents and heavy metal ions. This research gives important insights into the creation of effective and selective sorbents for heavy metal removal in water treatment applications.

(Hirotsu, 2006) describes a novel method for immobilizing cyclodextrin via plasma graft polymerization of glycidyl methacrylate. The author successfully grafts glycidyl methacrylate onto a substrate utilizing plasma treatment, followed by cyclodextrin immobilization. This paper shows the potential uses of this technology in numerous domains, such as medication delivery systems or separation science, providing a promising path for the production of functional materials with increased capabilities. The findings given in this work contribute to the improvement of surface modification techniques and encourage additional research in the field of polymer chemistry.

(Reddy et al., 2005)offer a unique method for improving the flame retardant qualities of cotton fabric using ionizing radiation graft polymerization and modification. The authors effectively show the efficiency of this technology in boosting the flame retardancy of cotton fabric, hence increasing its potential for usage in a variety of applications where fire safety is critical. This research adds to the improvement of materials science by providing significant insights into the production of flame-retardant fabrics. The findings provided in this research have major significance in industries such as clothes, home furnishings, and automotive fabrics, where fire-resistant qualities are critical.

In a nutshell, previous research has extensively examined metal adsorbents by graft polymerization for the treatment of industrial wastewater. This research has offered useful insights into monomer selection, grafting condition optimization, characterization methodologies, and performance evaluation of the resultant adsorbents. To improve the metal adsorption capability of the adsorbents, several monomers such as acrylic acid, methacrylic acid, acrylamide, and vinyl pyridine have been investigated. Previous research has also focused on optimizing grafting conditions such as temperature, reaction duration, initiator concentration, and pH. These factors are critical in defining the density and dispersion of the grafted polymer chains on cotton fibers, which influences the total adsorption capacity. The major findings of past investigations are summarized here.

1. (Nasef & Hegazy, 2004) used ionizing radiation to form an active radical in a fibrous trunk polymer, and the polymeric graft chains propagated from the active radical in the trunk polymer.
2. Various functional groups, such as iminodiacetic acid (Seko et al., 2005)and glutamine (Saito et al., 2004), have been grafted into polyethylene trunk polymer fibers.
3. In the case of fibrous adsorbents, (JYO et al., 2002) discovered that lead ions may be removed even at flow rates larger than 100(h-1).
4. Chemical grafting on cellulose has resulted in metal-ion adsorbents containing carboxy/amide functional groups (Okieimen et al., 2005), acrylamide (Biçak et al., 1999), and glucamine (Inukai et al., 2004).

Grafting of GMA onto cellulose has been accomplished using chemical agent initiation, plasma treatment, and mutual gamma irradiation (Hirotsu, 2006; Navarro et al., 2001; Reddy et al., 2005)

Chapter 3: METHODOLOGY

The number of industrial contaminants in our surroundings is continuously rising with financial and social growth which develops a significant environmental problem. These pollutants are responsible for deteriorating our health owing to their poisonousness and gathering in our body, mainly some heavy metals in waste, such as Cr, As, Pb, Hg,Fe and Cd (Jan et al., 2015). These heavy metals are non-decomposable in nature and cause di- verse health problems both in living organisms and sur- rounding environments. The elimination of heavy metals is now becoming an important concern because of their persistence within the atmosphere (Singh et al., 2011). Chromium is one of the major toxic metals after cadmium, lead, and mercury in the toxic metal list. It is found mainly in the trivalent, Cr (III) and hexavalent, Cr (VI) forms (Alemu et al., 2018). Trivalent chromium and elemental chromium appear comparatively.

In the methodology section, we outline the systematic approach taken to synthesize a biodegradable metal adsorbent through graft polymerization onto cotton, with the ultimate goal of treating industrial effluent. In this work, the synthesis of a biodegradable metal adsorbent was accomplished through graft polymerization onto cotton fibers. Cotton, being a natural and abundant material, provides an ideal substrate for the immobilization of the polymer chains. The graft polymerization process involves the attachment of functional monomers onto the cotton fibers, followed by the polymerization reaction to form a polymeric network (Purohit et al., 2023). This unique approach allows for the incorporation of metal-binding groups, enhancing the adsorption capacity of the cotton-based adsorbent (Wu et al., 2022).

Here, we intend to discuss the selection and preparation of cotton fibers, the choice of functional monomers, and the optimization of reaction conditions for graft polymerization. Detailed procedures for the characterization of the synthesized adsorbent, including Fourier-transform infrared (FTIR) spectroscopy will be outlined. Experimental parameters such as reaction time, temperature, and monomer concentration will be investigated to determine their impact on the adsorption performance of the biodegradable metal adsorbent.

3.1 MATERIALS AND REAGENTS

Pure cotton (Cellulose), Initiator Ceric ammonium nitrate (CAN), Monomer for grafting Glycidyl methacrylate (GMA), Crosslinking agent Tri-ethyl amine (TEA) and Ethylene diamine (EDA), Acetone, Nitric acid (HNO3), De-ionized water. Sodium hydroxide (NaOH), Hydrochloric acid (HCl), Buffer solution, Metal ions solution.

3.2 EQUIPMENTS

Reaction vessel, Magnetic stirrer, Heating Plate, UV-vis spectrophotometer, FTIR spectrophotometer, Balance, pH Meter, Drying Oven, Glassware and Laboratory Accessories. Safety Equipment, Water Bath, Centrifuge

3.3 GRAFTING OF POLY GLYCIDYL METHACRYLATE ON COTTON

Cotton Cellulose of 0.60g was immersed in 20 mL of water in a necked flask and the mixture was stirred at 50^0C for 30 minutes. Again 0.0548g CAN, 20mL 0.1M HNO_3, and GMA (1g, 1.2g, 1.5g, 2g, 2.5 g) were sequentially added to the reaction flask. The reaction flask was placed in a water bath and stirred for 30 minutes at 40^0C temperature. Then the reaction mixture dissolved in Acetone for 6 hours. Finally, cell-g-PGMA was obtained by drying under a vacuum at 60 ^0C for 24 hours. Figure 3.1 demonstrates the whole grafting procedure of polyglycidyl methacrylate on pure cotton.

The grafting percentages are presented in Table 3.1

The grafting percentage was calculated according to the Eq. 1.

Grafting percentage (G %),

$$=(\frac{A-B}{B})\times 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Here, A=weight of cell-g-PGMA and B=weight of Cotton

Table 3.1. Grafting percentage of cotton-*g*-PGMA with various concentrations of GMA

Sample	**Cotton(g)**	**GMA(g)**	**CAN(g)**	**Cell-g-PGMA**	**PGMA (G%)**
01	0.60	1	0.0548	1.33	121
02	0.60	1.20	0.0548	1.35	125
03	0.60	1.50	0.0548	1.5	140
04	0.60	2	0.0548	1.63	172
05	0.60	2.2	0.0548	1.8	200
06	0.60	2.5	0.0548	1.92	220

The whole process follows:

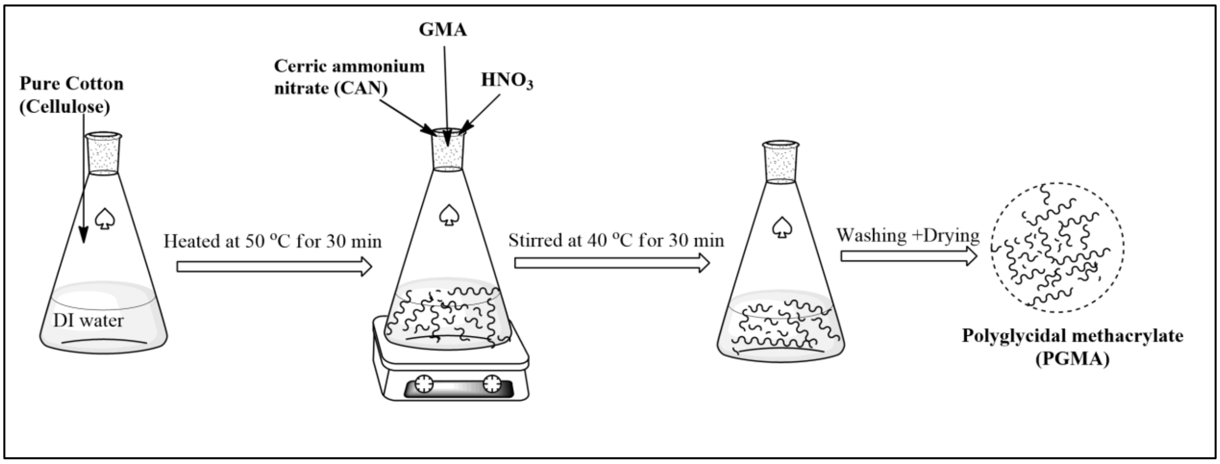


Figure 3.1 Synthesis procedure of cotton-g--PGMA

3.4 SYNTHESIS OF COTTON-GRAFTED-PTEAMA

1g powder of Cotton-g-PGMA was immersed in 50 mL of Acetone and 2g triethylamine in a necked flask and the mixture was stirred at 40^0C for 24 hours. Finally, 1.01g mass was obtained by drying under a vacuum at 60^0C for 24 hours which represented in the Figure 3.2. Percentage of yield=101%

The whole process follows:

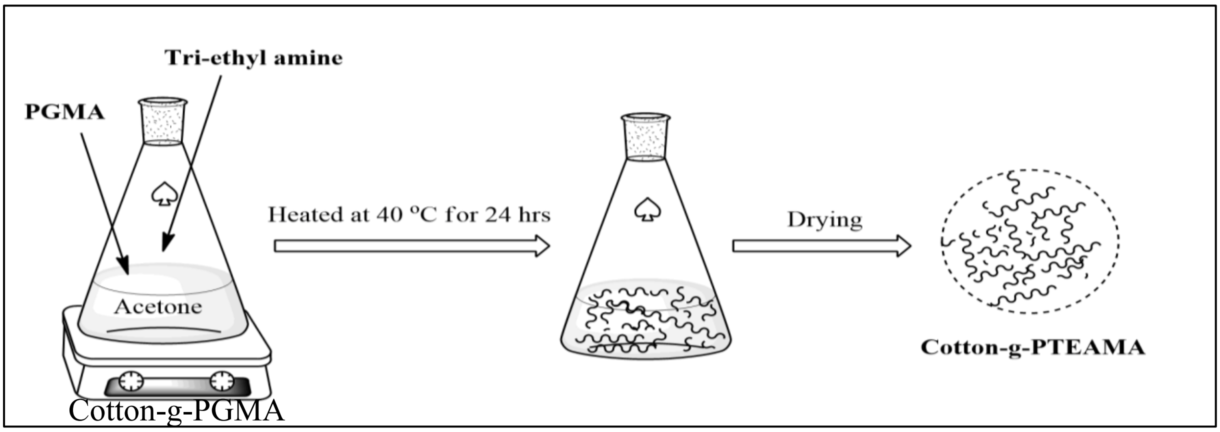


Figure 3.2 Synthesis procedure of cotton-g-PTEAMA

3.5 SYNTHESIS OF COTTON-GRAFTED-PEDAMA

0.42g powder of Cotton-g-PGMA was immersed in 50 mL of Acetone and 10mL of Ethylenediamine Anhydrous($C_2H_8N_2$) in a necked flask, and the mixture was stirred at 40^0C for 6 hours. Finally, 0.54g mass was obtained by drying under a vacuum at 60^0C for 24 hours shown in Figure 3.3. Percentage of yield=128.57%

The whole process follows:

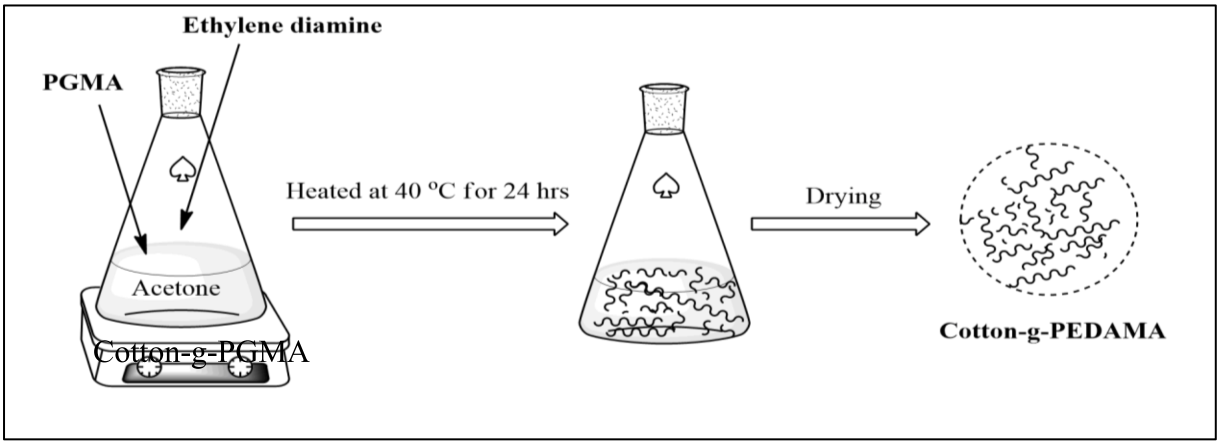


Figure 3.3 Synthesis procedure of cotton-g-PEDAM

3.6 ADSORPTION PROPERTIES OF COTTON-GRATED-PTEAMA AND COTTON-GRAFTED-PEDAMA

The adsorption properties of Cotton-*g*-PTEAMA and Cotton-g-PEDAMA investigated towards adsorption selective heavy metals chromium (Cr) and iron (Fe) from their aqueous solution. For the adsorption studies different initial concentrations of these metal ions solution were prepared by diluting the standard solution (1000 ppm) of Cr and Fe. These adsorption studies were conducted in a shaking water bath with 100-150 oscillations per minute. 1g of adsorbent added to 1000 mL of each metal solution and continued the experiment in a shaking water bath at room temperature till adsorption reached equilibrium. The concentration of metal solution before and after adsorption process was observed using Visible spectrophotometer and observing the physical colour appearance of these metal ions solution. And the adsorption efficiency calculated using the following Eq. 2

$$\text{Adsorption (\%)} = \frac{C_0 - C_t}{C_0} \times 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 2$$

where, C_0 = the initial concentration and

C_t = the concentration at time t.

Chapter 4: RESULTS AND DISCUSSION

A thorough understanding of the efficacy and ramifications of the created adsorbent is offered by chapter four. Results from a variety of analyses, such as the characterization of the modified cotton, Infrared spectrum, adsorption efficiency, and material attributes, are presented in the results section. The modified cotton, featuring graft polymerization with PGMA, exhibits enhanced properties for metal adsorption (Zhang et al., 2021). The results include data on the structural changes, and the presence of functional groups introduced during the grafting process. Analytical techniques such as FTIR (Fourier Transform Infrared Spectroscopy) is employed for a detailed characterization.

The adsorption efficiency results are the focal point of the discussion. Data on the removal of targeted metals, such as Chromium (Cr) and Iron (Fe), from industrial effluent, is presented and compared to assess the effectiveness of the adsorbent. Factors influencing adsorption, such as pH, contact time, reading (ppm), dilution and initial metal concentration are discussed to understand the optimal conditions for the process.

4.1 SYNTHESIS AND CHARACTERIZATION OF COTTON-G-PGMA

The GMA grafted on pure cotton through condensation polymerization to prepare a modified co-polymer of cellulose which further functionalized with tri-ethyl amine by the nucleophilic ring opening addition of the amine derivatives to the epoxy rings. The Cotton-*g*-PGMA and pure Cotton were characterized using Fourier transform infrared (FT-IR) spectroscopic analysis Figure 4.1. For the carbonyl moieties and epoxy moieties the characteristic absorption band peaks appeared at 1721 cm^{-1} and 905 cm^{-1}, 845 cm^{-1} respectively in FT-IR spectrum of cotton-*g*-PGMA Figure 4.2, these characteristic band peaks are not present in the spectrum of the pure cotton. Appearance of absorption peaks for epoxy and carbonyl moieties ensured the grafting process was successfully completed.

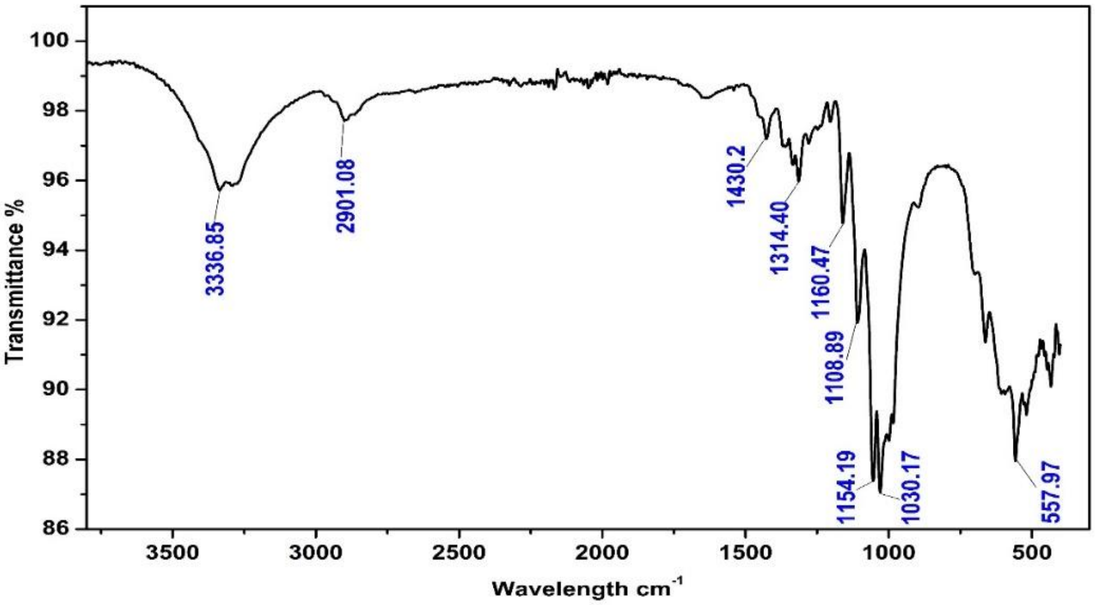


Figure 4.1 FT-IR spectra of pure cotton

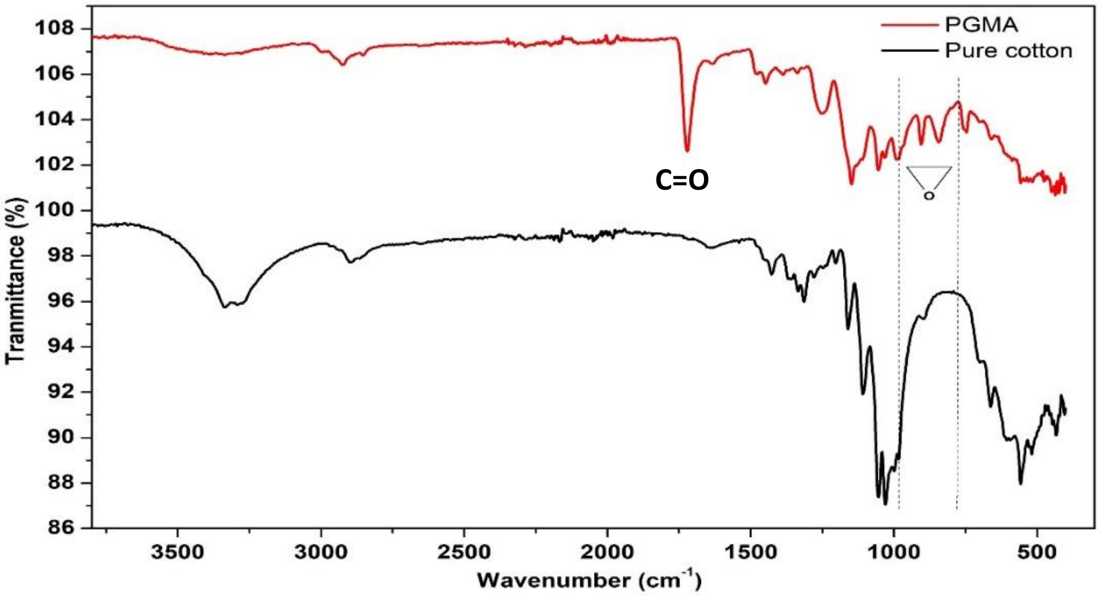


Figure 4.2 FT-IR spectra of pure cotton and cotton-g-PTEAMA

4.2 SYNTHESIS AND CHARACTERIZATION OF COTTON-G-PTEAMA

1g powder of Cotton-g-PGMA was immersed in 50 mL of Acetone and 2g triethylamine in a necked flask and the mixture was stirred at 40^0C for 24 hours. Finally, 1.01g mass was obtained by drying under a vacuum at 60^0C for 24 hours. The following reactions are occurred which are presented with pictures in Figure 4.3.

The whole reaction process are as follows:

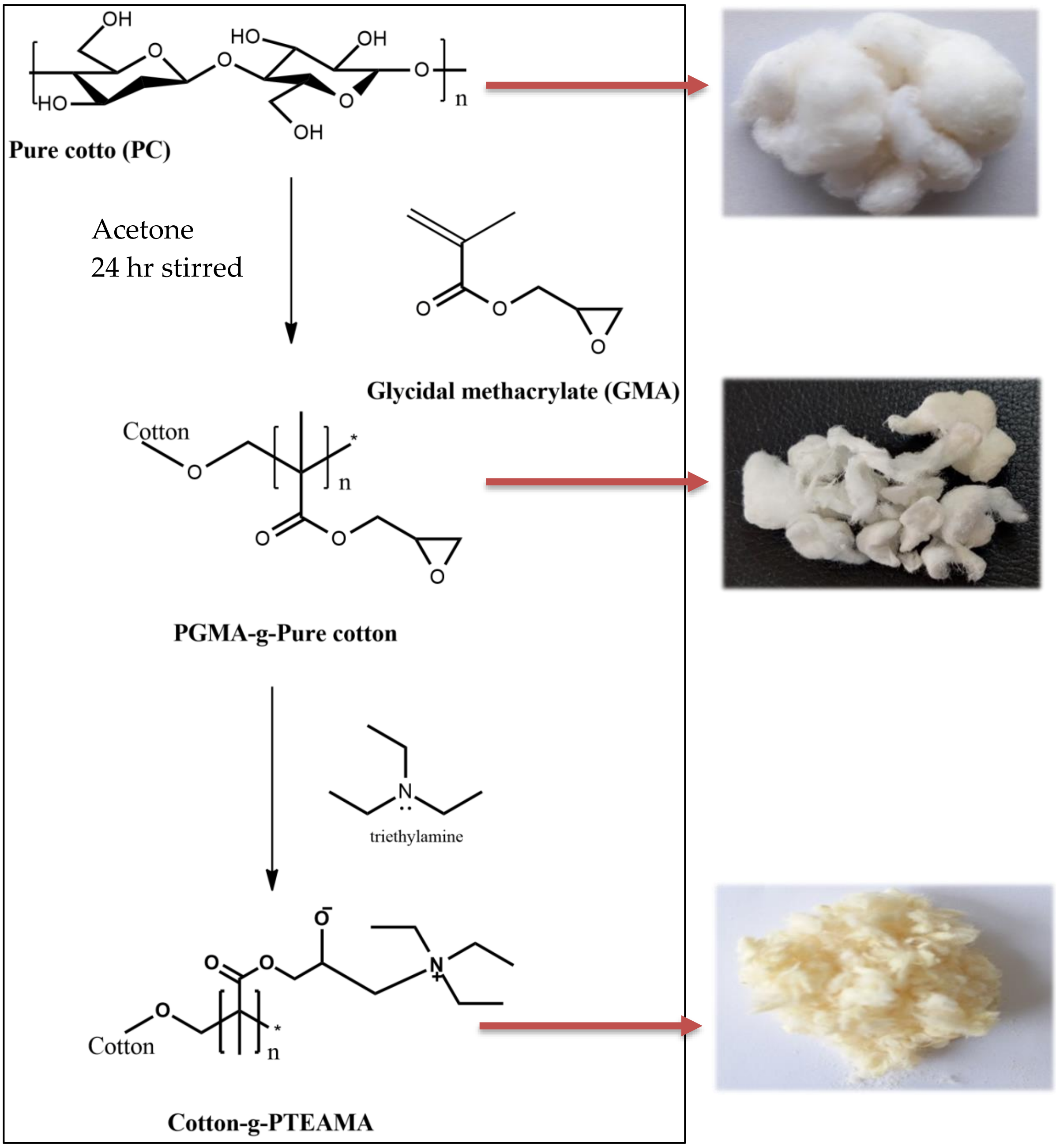


Figure 4.3 Reaction scheme of cotton-g-PTEAMA

The GMA grafted on pure cotton through condensation polymerization to prepare modified co-polymer of cellulose which further functionalized with tri-ethyl amine by the nucleophilic ring opening addition of the amine derivatives to the epoxy rings. The Cotton-*g*-PGMA and Cotton-*g*-PTEAMA were characterized using Fourier transform infrared (FT-IR) spectroscopic analysis represented in the Figure 4.4. For the carbonyl moieties and epoxy moieties the characteristic absorption band peaks appeared at 1721 cm^{-1} and 905 cm^{-1}, 845 cm^{-1} respectively in FT-IR spectrum of cotton-*g*-PGMA, these characteristic band peaks are not present in the spectrum of the Pure cotton. In the spectrum of Cotton-*g*-PTEAMA characteristic peak for amine moieties appeared at 1566 cm^{-1} and the peaks of epoxy ring disappeared because of the reaction takes place in the epoxy ring with tri-ethyl amine during functionalizing cotton-*g*-PGMA.

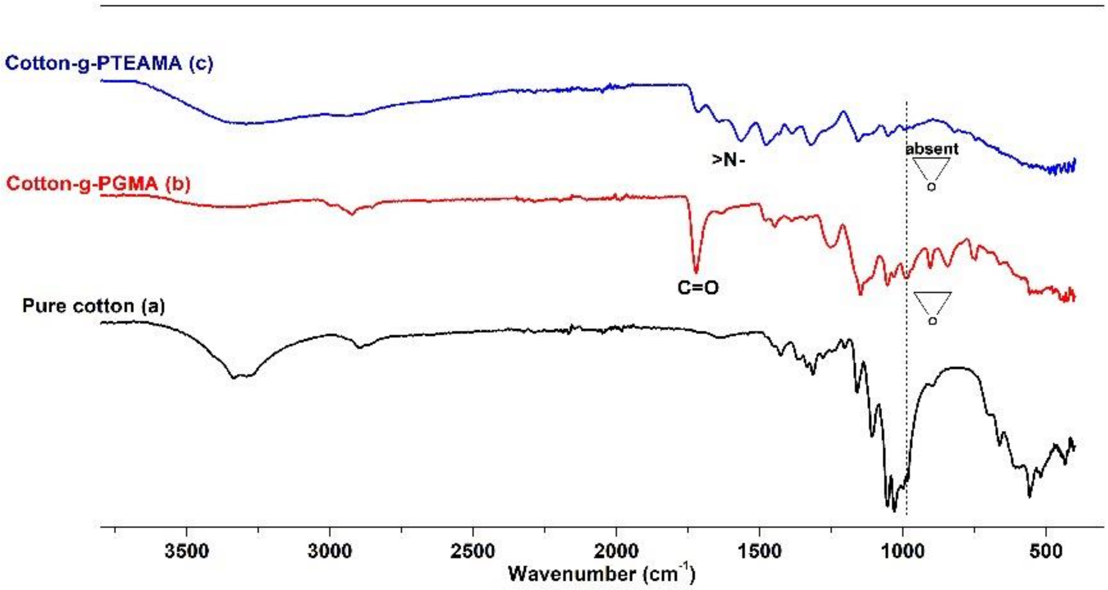


Figure 4.4 FT-IR spectra of pure cotton, cotton-g-PGMA and cotton-g-PEDAMA

4.3 SYNTHESIS AND CHARACTERIZATION OF COTTON-G-PEDAMA

0.42g powder of Cotton-g-PGMA was immersed in 50 mL of Acetone and 10mL of Ethylenediamine Anhydrous in a necked flask, and the mixture was stirred at 40⁰C for 6 hours. Finally, 0.54g mass was obtained by drying under a vacuum at 60⁰C for 24 hours. The following reaction are occurred which are presented with pictures in Figure 4.5.

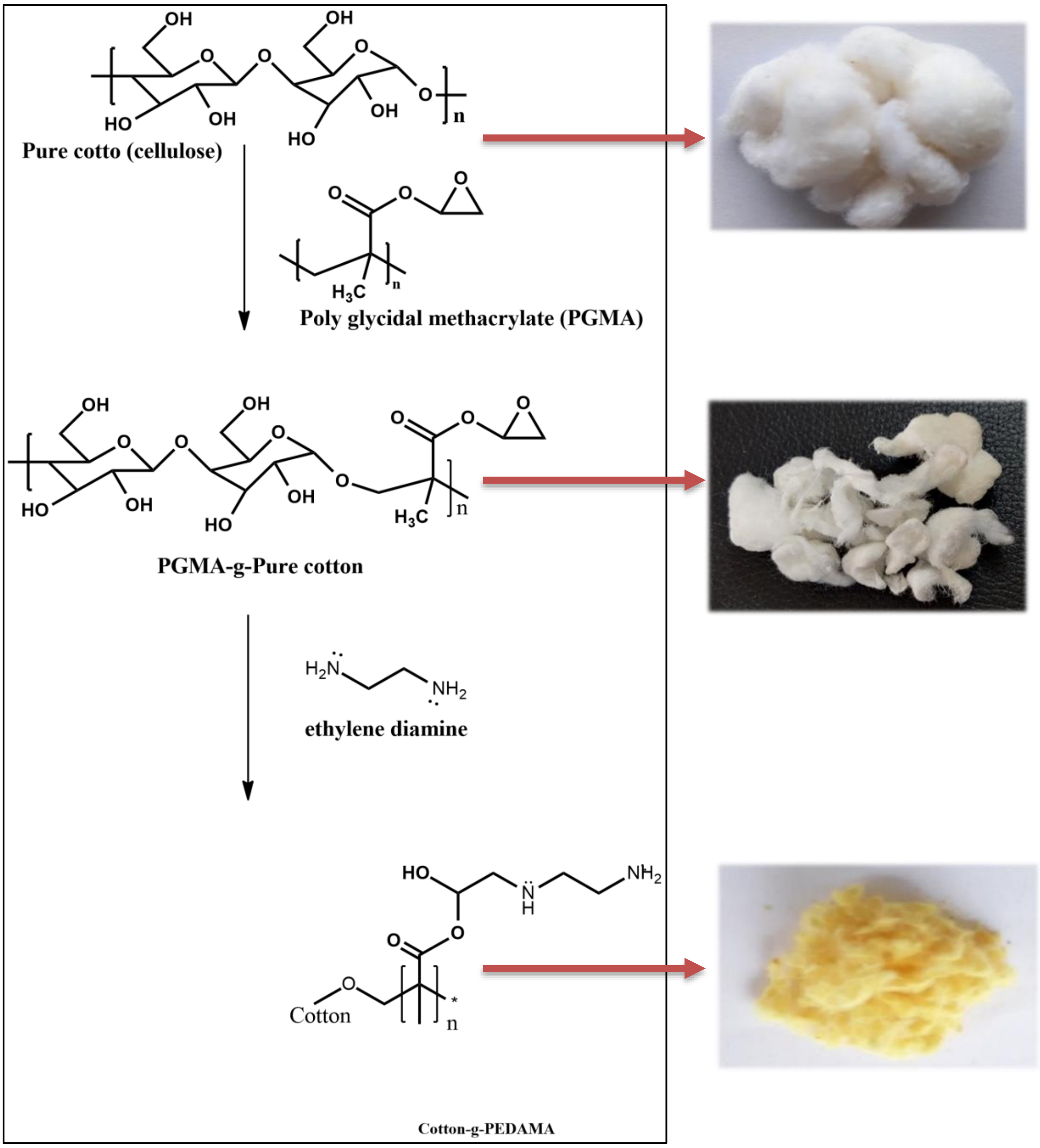


Figure 4.5 Reaction scheme of cotton-g-PEDAMA

The GMA grafted on pure cotton through condensation polymerization to prepare modified co-polymer of cellulose which further functionalized with tri-ethyl amine by the nucleophilic ring opening addition of the amine derivatives to the epoxy rings. The Cotton-*g*-PGMA and Cotton-*g*-PEDAMA were characterized using Fourier transform infrared (FT-IR) spectroscopic analysis represented in Figure 4.6. For the carbonyl moieties and epoxy moieties the characteristic absorption band peaks appeared at 1721 cm^{-1} and 905 cm^{-1}, 845 cm^{-1} respectively in FT-IR spectrum of cotton-*g*-PGMA, these characteristic band peaks are not present in the spectrum of the Pure cotton. In the spectrum of Cotton-*g*-PEDAMA characteristic peak for amine moieties appeared at 1566 cm^{-1} and the peaks of epoxy ring disappeared because of the reaction takes place in the epoxy ring with Ethylene diamine during functionalizing cotton-*g*-PGMA.

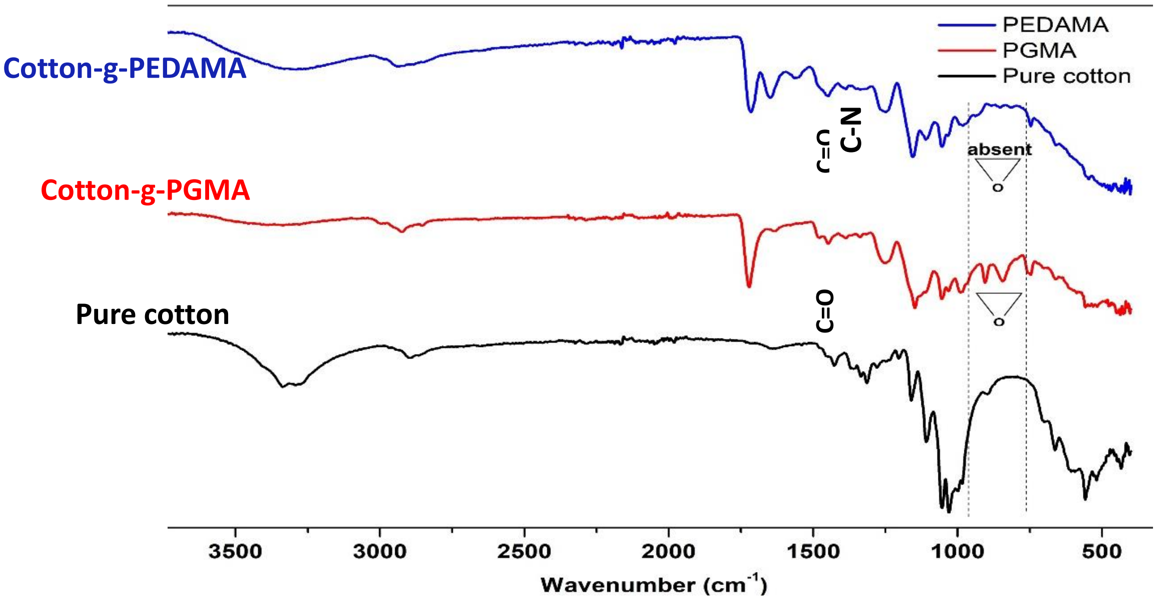


Figure 4.6 FT-IR spectra of pure cotton, cotton-g-PGMA and cotton-g-PEDAMA

4.4 ADSORPTION STUDIES OF COTTON-GRAFTED-PTEAMA

4.4.1 Effect of pH

Effect of pH studies investigated for the adsorption of Cr and Fe ions by cotton-*g*-PTEAMA adsorbent demonstrated the result in Figure 4.7. For this experiment the pH of the following metal solution adjusted in the range 2-10 by 0.1N HNO_3 and 0.1N NaOH solutions. Cotton-*g*-PTEAMA added into Cr and Fe solutions with pH being maintained constant for 5 hours where equilibrium reaches and further continued the shaking for 24 hours in the shaking water bath. The adsorption of Fe by Cotton-*g*-PTEAMA was found to be higher with the increasing pH of the metal solution with the significant change after pH 4 while in the other hand adsorption of Cr with the increase of pH showed a decreasing property. At the lower pH there are many H^+ ions present in the solution compete with Fe^{2+} ions and accumulate with the negative sites of adsorbent resultant less interaction with the Fe^{2+} ions. Also, at lower pH level the availability of Fe^{2+} ions decrease hence less adsorption showed by the adsorbent. But with the increasing pH the H^+ ions become lesser in the solution where the number of Fe^{2+} ions increase hence adsorption in increased.

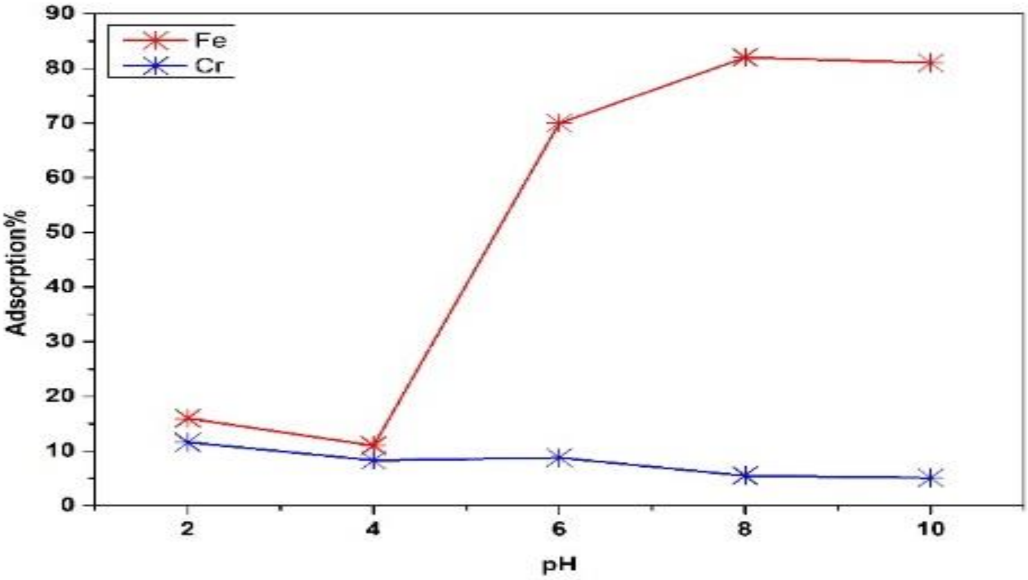


Figure 4.7 Effect of pH on adsorption of cotton-g-PTEAMA

On the other hand, adsorption of Cr by cotton-*g*-PTEAMA decreased with the increase of pH value. This phenomenon occurred due to less availability of Cr^{3+} ions in the solution when pH getting higher its resultant higher number of OH^- species in the solution. With this phenomena precipitation occurs hydrolysed species of chromium because of their less solubility in alkaline environment hence less Cr^{3+} ions available in the solution adsorption decreased. So, in higher pH level adsorption of Fe become higher and Cr become lower by prepared cotton-*g*-PTEAMA.

4.4.2 Isotherm studies

To evaluate the adsorption efficiency and mechanism of adsorption isotherm adsorption studies investigated. Adsorption isotherm studies inspects the uptake capacity of adsorbent with different initial concentration of adsorbate Figure and also examine the interaction of adsorbent with adsorbates. The adsorption isotherm studies investigated for the experimental adsorption equilibrium uptakes (q_e) data for Cr and Fe by cotton-*g*-PTEAMA, these data were analysed with two adsorption models: Langmuir Eq. 1 and Freundlich Eq. 2 isotherm models and also demonstrated in the Figure 4.9.

$$\frac{C_e}{q_e} = \frac{1}{K_l q_m} + \frac{C_e}{q_m} \qquad (1)$$

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \qquad (2)$$

where C_e (mg L^{-1}) is the equilibrium concentration of metal ions in solution, q_e (mg g^{-1}) is the amount of metal ion adsorbed at equilibrium, q_m (mg g^{-1}) is the maximum adsorption capacity, K_l (L g^{-1}) is the Langmuir adsorption equilibrium constant related to adsorption energy, K_f (L g^{-1}) is the Freundlich adsorption equilibrium constant related to adsorption capacity, and n is an empirical parameter related to the adsorption intensity. Langmuir model Eq. (1) assumes that there is no interaction occurs between absorbent and adsorbed molecules.

Resultant a single monolayer adsorption takes place when the adsorbed molecules get homogeneously saturated on the surface of the adsorbent and there a definite number of binding sites present on the adsorbent. The adsorption won't be influenced further by the transportation of solutes when monolayer adsorption completes. Freundlich model Eq. (2) is exponential equation describes the concentration of the adsorbates increases on the surface of adsorbent while the concentration of adsorbates being increased in their solution. Adsorption capacity increased with increase of initial concentration for Fe showed in Figure 4.8

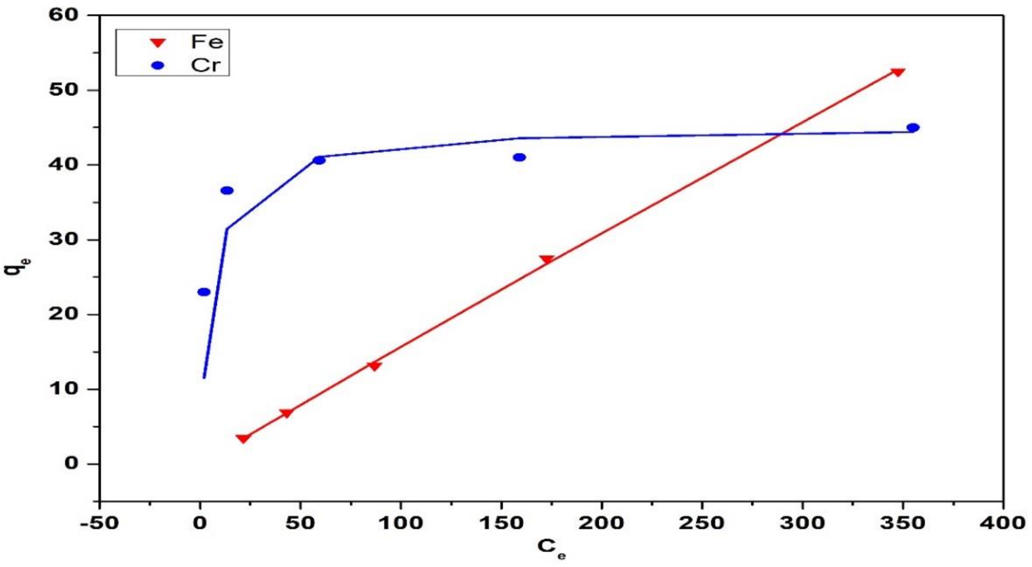


Figure 4.8 Effect of different initial concentration

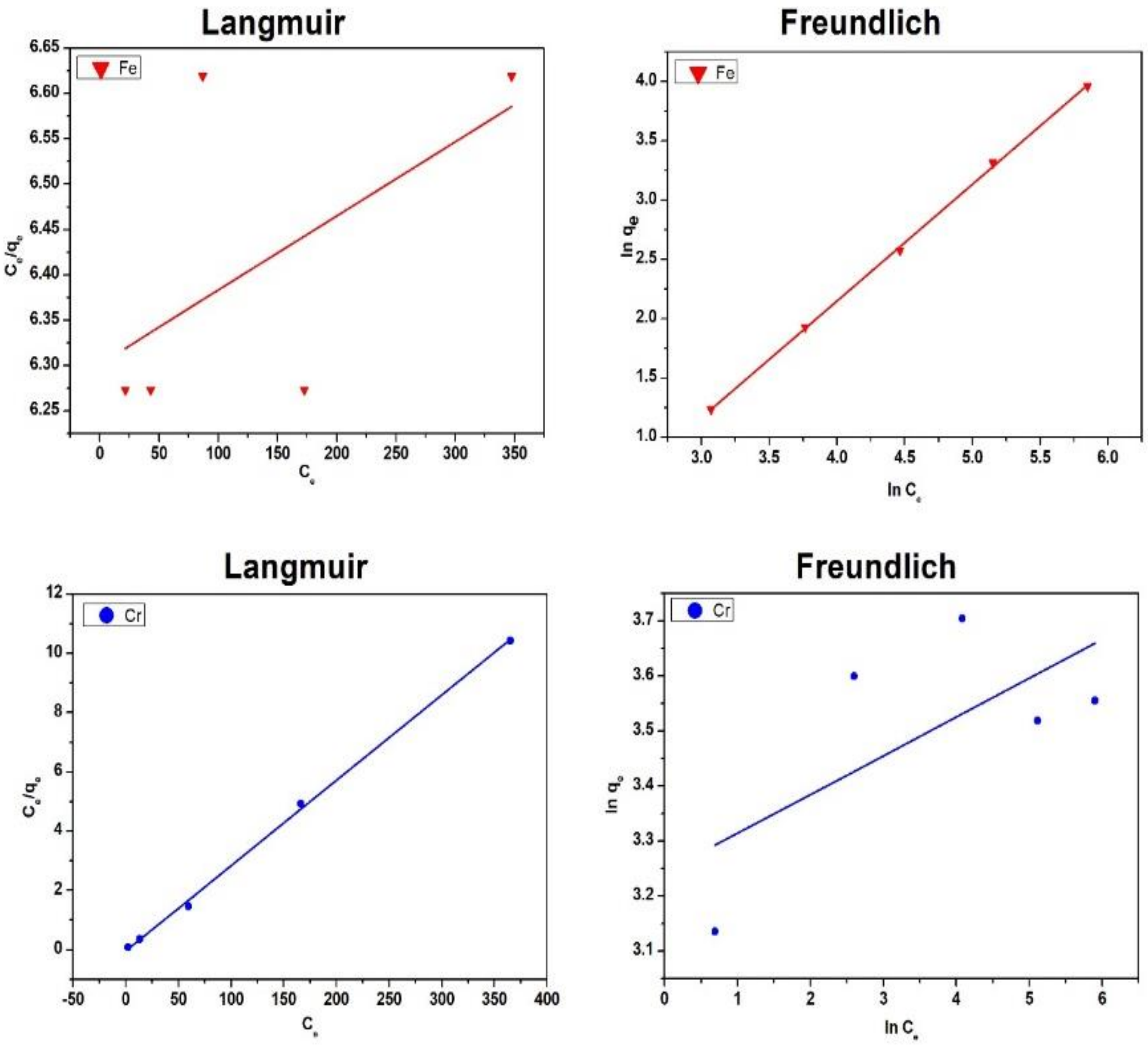


Figure 4.9 Linear plots of Langmuir and Freundlich isotherm models of adsorption of Fe and Cr by cotton-*g*-PTEAMA. Conditions: initial concentration of Cr and Fe ions, 25-400 mgL^{-1}; cotton-*g*-PTEAMA, 1 gL^{-1}; pH 6.0, 25 ^{0}C, 24 h

Table 4.1. Isotherm co-efficient for adsorption of metals by cotton-*g*-PTEAMA

Metal	**Langmuir**			**Freundlich**		
	q_m	K_l	R^2	K_f	n	R^2
Fe	12.68	0.0001	0.571	0.1672	1.0157	0.999
Cr	34.72	0.7868	0.999	25.6255	14.1964	0.674

Freundlich isotherm model usually describes a heterogenous system and the characteristics of adsorption. Following experimental data were investigated for both models and the R^2 values indicates the better fitting of these experimental data to both consecutive models. Important parameters associated with both models tabulated in the Table 4.1. Adsorption of Fe by Cotton-*g*-PTEAMA showed best fitting to Freundlich isotherm model with the R^2 value 0.9997 and adsorption of Cr showed best fitting to Langmuir isotherm model with the R^2 value 0.9994 represented in the Figure 4.9. Linearity of these experimental data to both models exhibit the adsorption nature towards Fe and Cr by synthesized Cotton-*g*-PTEAMA adsorbent.

4.4.3 Kinetics studies

Adsorption of Fe and Cr by Cotton-*g*-PTEAMA investigated with kinetics models pseudo first order Eq. (3) and pseudo second order Eq. (4) to evaluate the adsorption efficiency with respect to time.

$$\ln(q_e - q_t) = \ln q_e - k_1 t) \qquad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (4)$$

where qe (mg g^{-1}) and qt (mg g^{-1}) are the mass of adsorbed metal ions per unit mass of the adsorbent at equilibria and time (t), respectively, and k_1 (g mg^{-1} min^{-1}) and k_2 (dm^{-3} mg^{-1} min^{-1}) are the rate constants of pseudo-first-order and pseudo second-order models, respectively.

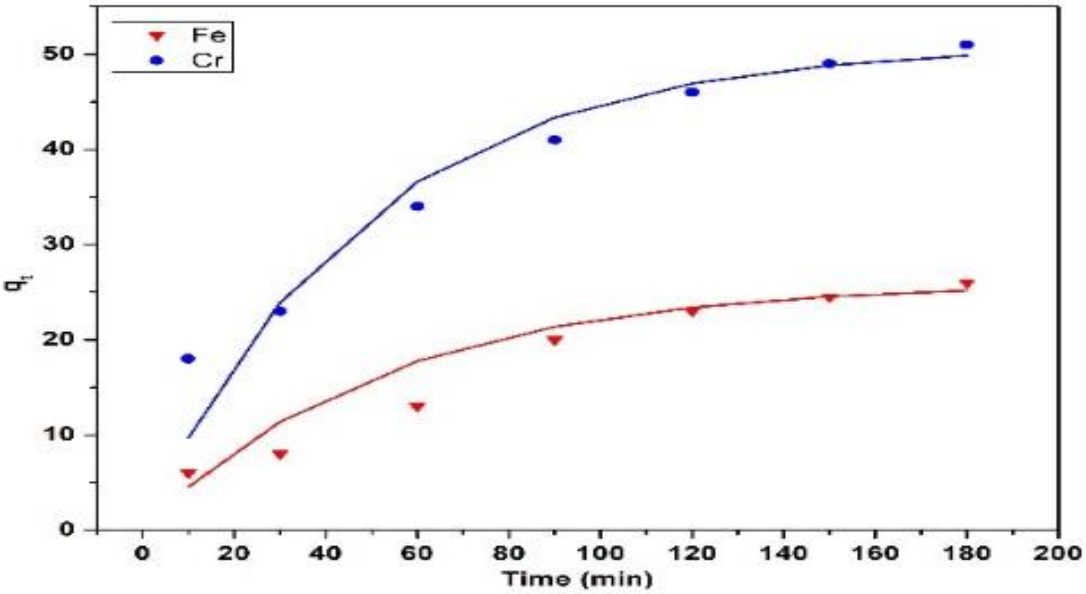


Figure 4.10 Adsorption kinetics of Fe and Cr by cotton-*g*-PTEAMA. Conditions: initial concentration Cr and Fe, 50 mgL^{-1}; cotton-*g*-PTEAMA,1 gL^{-1};pH 6.0,25 ^0C, pH, 6.

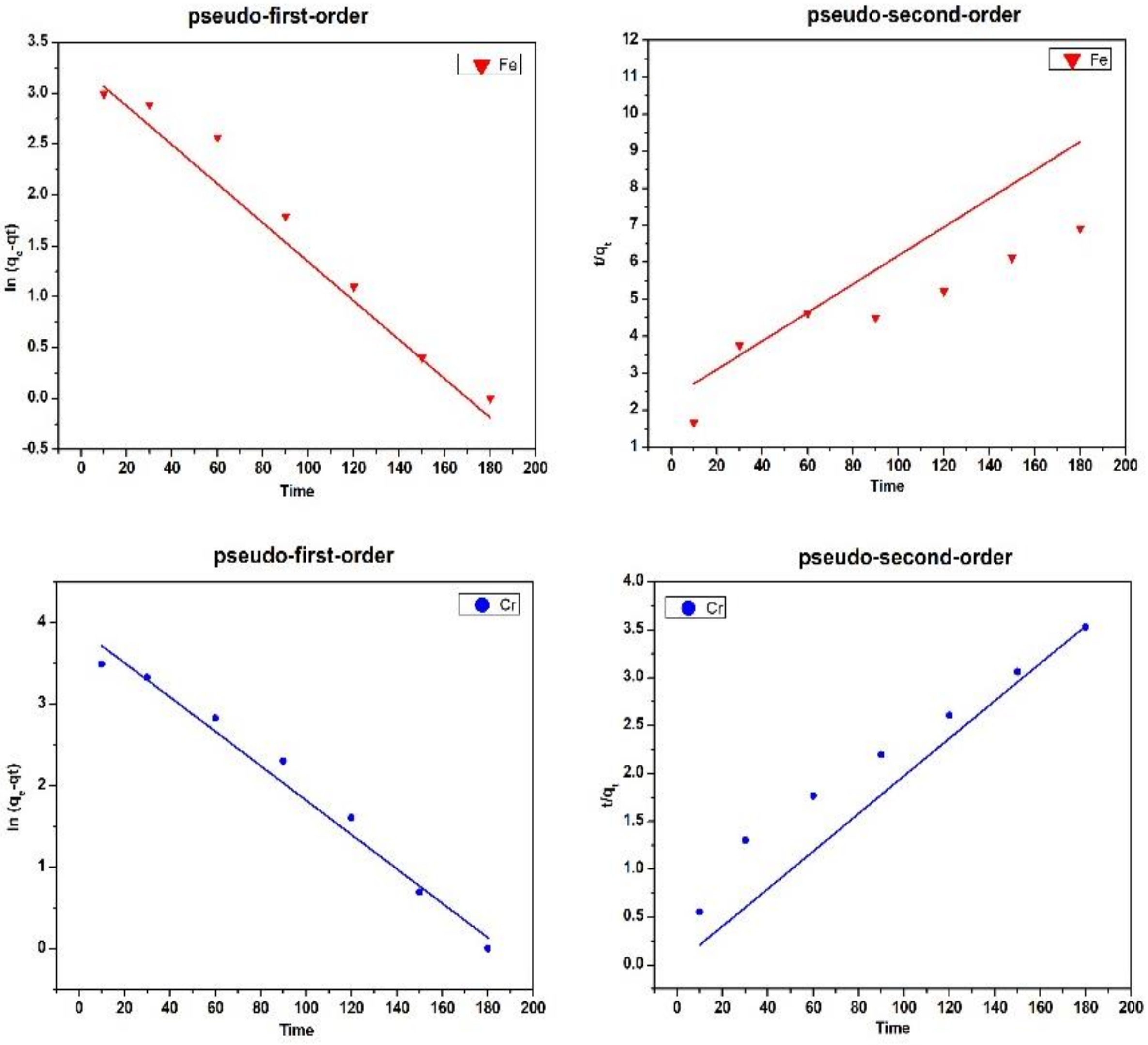


Figure 4.11 Linear plots of pseudo-first order and pseudo-second-order model for adsorption of Fe and Cr by cotton-*g*-PTEAMA. Conditions: initial concentration of Cr and Fe ions, 50 mgL^{-1}; cotton-*g*-PTEAMA, 1 gL^{-1}; pH 6.0, 25 ^{0}C

The kinetics model studies interpret with experimental data and exhibit the dynamic characteristics of adsorption of Fe and Cr by Cotton-g-PTEAMA. The metal uptake capacity (qt, mg/g) for the kinetic data calculated using the following eq. 5 and represented in the Figure 4.10

$$q_t = \frac{(C_0 - C_t)v}{m} \qquad (5)$$

where C_t and C_0 are concentrations (mg^{L-1}) at time t and 0 respectively and v represents the solution volume (L), and m is the adsorbents mass. In the kinetics studies, Figure 4.11 demonstrate the correlation of experimental data with both kinetics model for adsorption of Fe and Cr, hence adsorption of Fe showed best fitting to pseudo first order model and adsorption of Cr showed best fitting also to pseudo first order model with R^2 values 0.9901 and 0.9900 respectively. The important parameters related with these kinetic models e.g. The rate constants, linear correlation coefficients (R^2), and both experimental (q_e, exp) and calculated (q_e, cal) uptake values for Fe and Cr metals are represented in Table 4.2

Table 4.2. Kinetics co-efficient for adsorption of metals by cotton-*g*-PTEAMA

Metal	**Pseudo first order**				**Pseudo second order**			
	K_1 (min^{-1})	R^2	qe, cal (mg/g)	qe, exp	K_2 (min^{-1})	R^2	qe, cal (mg/g)	qe, exp
Fe	0.0006	0.9901	26	19.4	0.0191	0.9442	26	25.7
Cr	0.0210	0.9900	51	49.85	0.0298	0.9803	51	50.81

4.4.4 Reusability of Cotton-g-PTEAMA

From the commercial view of point using 3 different desorbing agents the reuse and regeneration investigated according adsorption-desorption capacity of cotton-g-PTEAMA showed in Figure 4.12. This investigation shows that maximum desorption capacity acquired with 0.5M HNO_3 solution for both metals Fe and Cr where other two desorption agents 0.5M NaOH and 0.5M HCl showed lesser efficiency. Maximum desorption efficiency obtained by 0.5M HNO_3 for cotton-g-PTEAMA is about 85% for Fe and 54.5% for Cr adsorption. Hence this experiment demonstrated that regeneration of adsorption capacity of cotton-g-PTEAMA can be retained with HNO_3 concurring maximum efficiency.

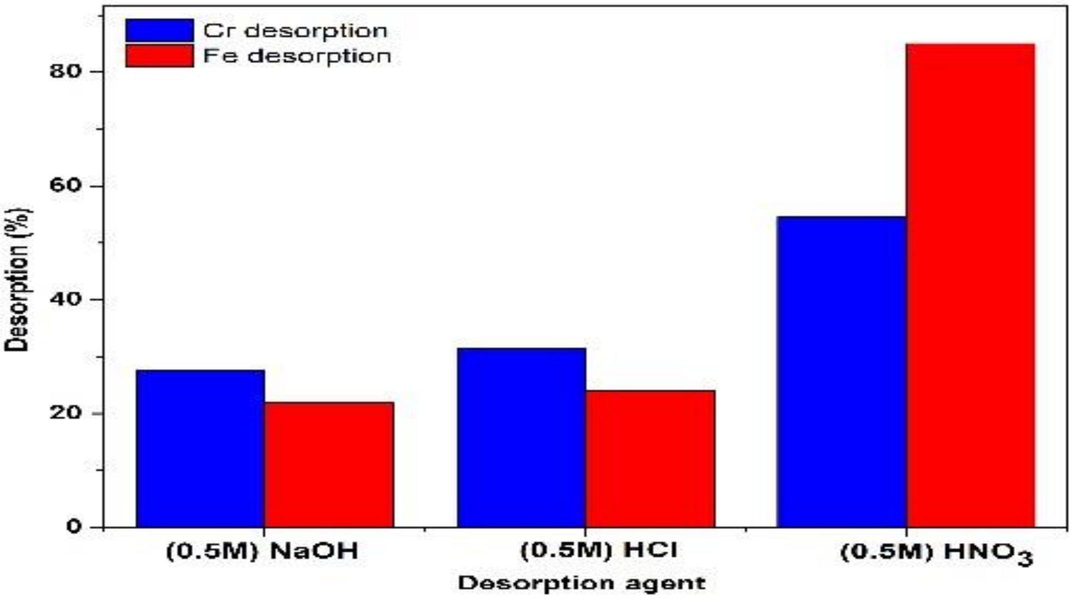


Figure 4.12 Desorption percentage by three desorbing agents 0.5M NaOH, 0.5M HCl and 0.5M HNO_3

To evaluate the reusability characteristics of cotton-g-PTEAMA the adsorption desorption process continued for 5 number of cycles. Figure 4.13 demonstrate the adsorption efficiency after 5 cycles of adsorption and desorption process. Adsorption of Fe by cotton-g-PTEAMA was above 10% initially which tends to increase after first cycle. And adsorption of Cr by cotton-g-PTEAMA was about 40% at the initial stage which decreased after the first cycle. This analysis shows the reusability and amount of adsorption capacity retained after some individual number of cycles of adsorption and desorption.

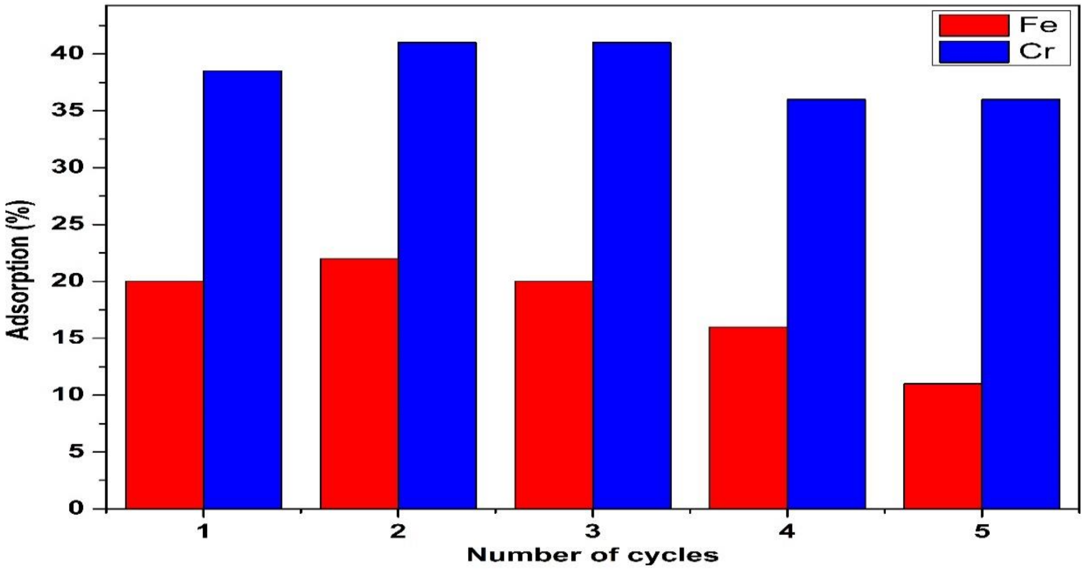


Figure 4.13 Reusability of cotton-g-PTEAMA

4.4.5 Industrial application of Cotton-g-PTEAMA

Two samples were prepared containing Fe and Cr. Concentration of Fe and Cr was maintained same as reported in the literature. Solutions was prepared that contains Fe and Cr metals. Cotton-g-PTEAMA added into solution to adsorb metals from the solution mixture. Concentration of metal solution determined after the adsorption process and calculated the adsorption efficiency by percentage of adsorption. Adsorbent= 1g/L; 25 °C, 24 hr, pH= 6. Showed good Cr removal efficiency from samples-01 and also sample-02. Experimental data and graph are represented in the Table 4.3 and Figure 4.14 respectively.

Table 4.3. Adsorption of metals by cotton-*g*-PTEAMA from industrial samples

Absorbent Cotton-g-PTEAMA

Sample	Components	Concentration (ppm)	Final concentration (ppm)	Adsorption (ppm)	Adsorption %
1	Fe	20.00	12.40	7.6	38
	Cr	0.12	0.02	0.1	83.33
2	Fe	45.00	22.50	22.5	50
	Cr	0.12	0.008	0.112	93.33

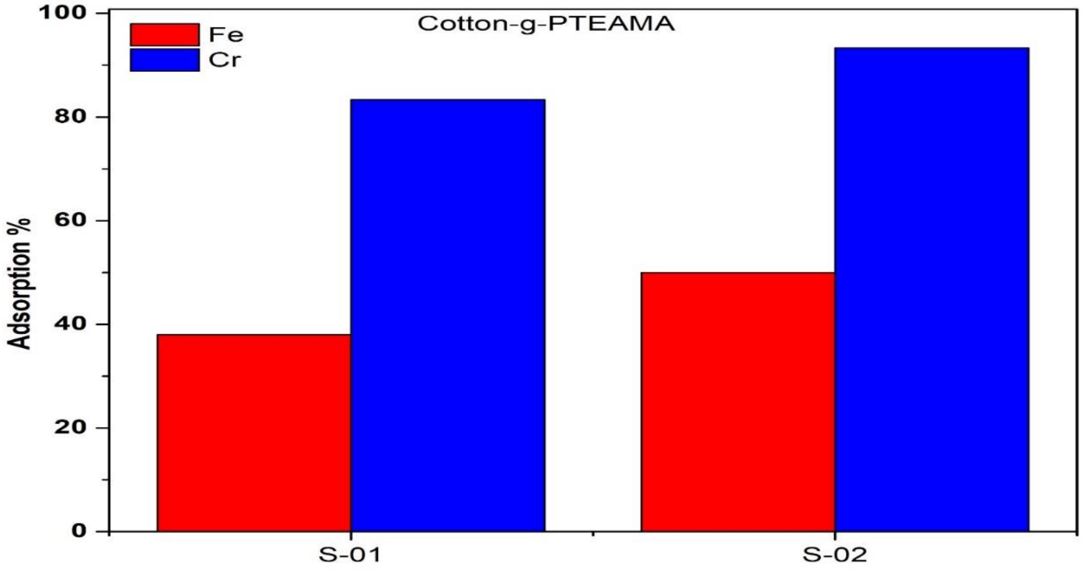


Figure 4.14 Comparative adsorption diagram of Fe and Cr about Sample-01 and Sample-02 for industrial applications

4.5 ADSORPTION STUDIES OF COTTON-GREAFTED-PEDAMA

4.5.1 Effect of pH

Effect of pH studies investigated for the adsorption of Cr and Fe ions by cotton-*g*-PEDAMA adsorbent Figure 4.15. For this experiment the pH of the following metal solution adjusted in the range 2-10 by 0.1N HNO_3 and 0.1N NaOH solutions. Cotton-*g*- PEDAMA added into Cr and Fe solutions with pH being maintained constant for 5 hours where equilibrium reaches and further continued the shaking for 24 hours in the shaking water bath. The adsorption of Fe by Cotton-*g*- PEDAMA was found to be higher with the increasing pH of the metal solution with the significant change after pH 4 while in the other hand adsorption of Cr with the increase of pH showed a decreasing property. At the lower pH there are many H^+ ions present in the solution compete with Fe^{2+} ions and accumulate with the negative sites of adsorbent resultant less interaction with the Fe^{2+} ions. Also, at lower pH level the availability of Fe^{2+} ions decrease hence less adsorption showed by the adsorbent. But with the increasing pH the H^+ ions become lesser in the solution where the number of Fe^{2+} ions increase hence adsorption in increased.

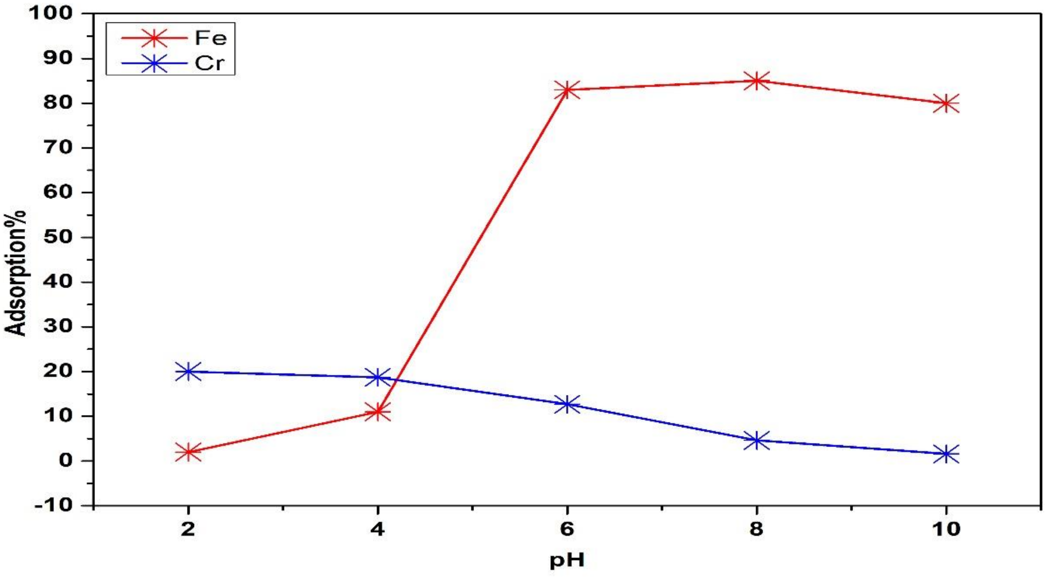


Figure 4.15 Effect of pH on adsorption of cotton-g-PEDAMA

On the other hand, adsorption of Cr by cotton-*g*- PEDAMA decreased with the increase of pH value. This phenomenon occurred due to less availability of Cr^{3+} ions in the solution when pH getting higher its resultant higher number of OH^- species in the solution. With this phenomena precipitation occurs hydrolysed species of chromium because of their less solubility in alkaline environment hence less Cr^{3+} ions available in the solution adsorption decreased. So in higher pH level adsorption of Fe become higher and Cr become lower by prepared cotton-*g*- PEDAMA.

4.5.2 Isotherm studies

To evaluate the adsorption efficiency and mechanism of adsorption isotherm adsorption studies investigated. Adsorption isotherm studies inspects the uptake capacity of adsorbent with different initial concentration of adsorbate Figure and also examine the interaction of adsorbent with adsorbates. The adsorption isotherm studies investigated for the experimental adsorption equilibrium uptakes (q_e) data for Cr and Fe by cotton-*g*- PEDAMA, these data were analysed with two adsorption models: Langmuir Eq (6). and Freundlich Eq (7). And isotherm models demonstrate in the Figure 4.17.

$$\frac{C_e}{q_e} = \frac{1}{K_l q_m} + \frac{C_e}{q_m} \qquad (6)$$

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \qquad (7)$$

where C_e (mg L^{-1}) is the equilibrium concentration of metal ions in solution, q_e (mg g^{-1}) is the amount of metal ion adsorbed at equilibrium, q_m (mg g^{-1}) is the maximum adsorption capacity, K_l (L g^{-1}) is the Langmuir adsorption equilibrium constant related to adsorption energy, K_f (L g^{-1}) is the Freundlich adsorption equilibrium constant related to adsorption capacity, and n is an empirical parameter related to the adsorption intensity. Langmuir model eq. (6) assumes that there is no interaction occurs between absorbent and adsorbed molecules.

Resultant a single monolayer adsorption takes place when the adsorbed molecules get homogeneously saturated on the surface of the adsorbent and there a definite number of binding sites present on the adsorbent. The adsorption won't be influenced further by the transportation of solutes when monolayer adsorption completes. Freundlich model eq. (7) is exponential equation describes the concentration of the adsorbates increases on the surface of adsorbent while the concentration of adsorbates being increased in their solution. Adsorption capacity increased with increase of initial concentration for both Fe and Cr. Which is presented in the Figure 4.16.

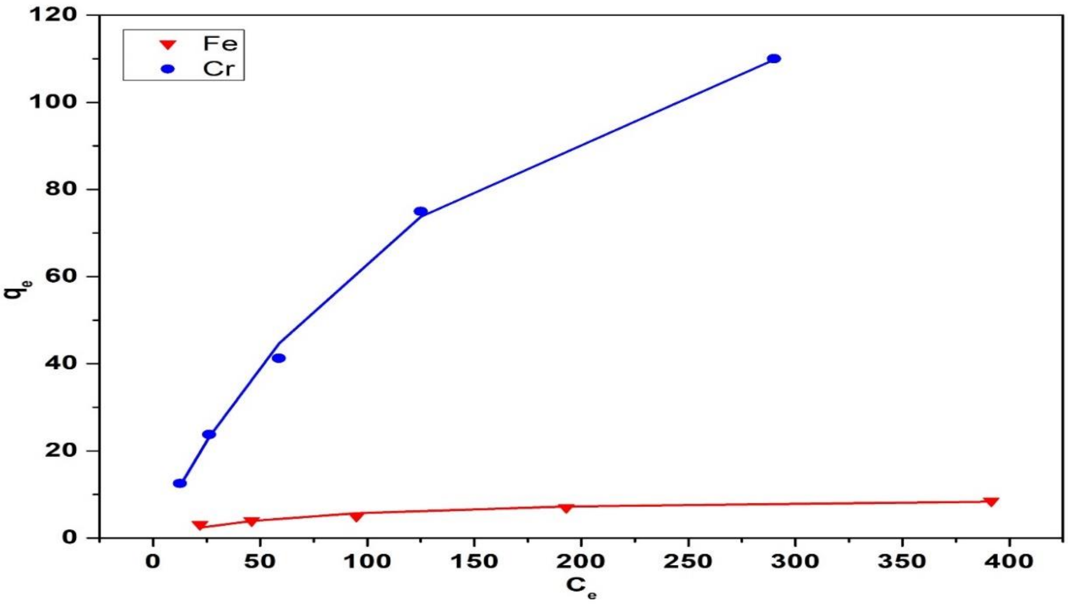


Figure 4.16 Effect of different initial concentration

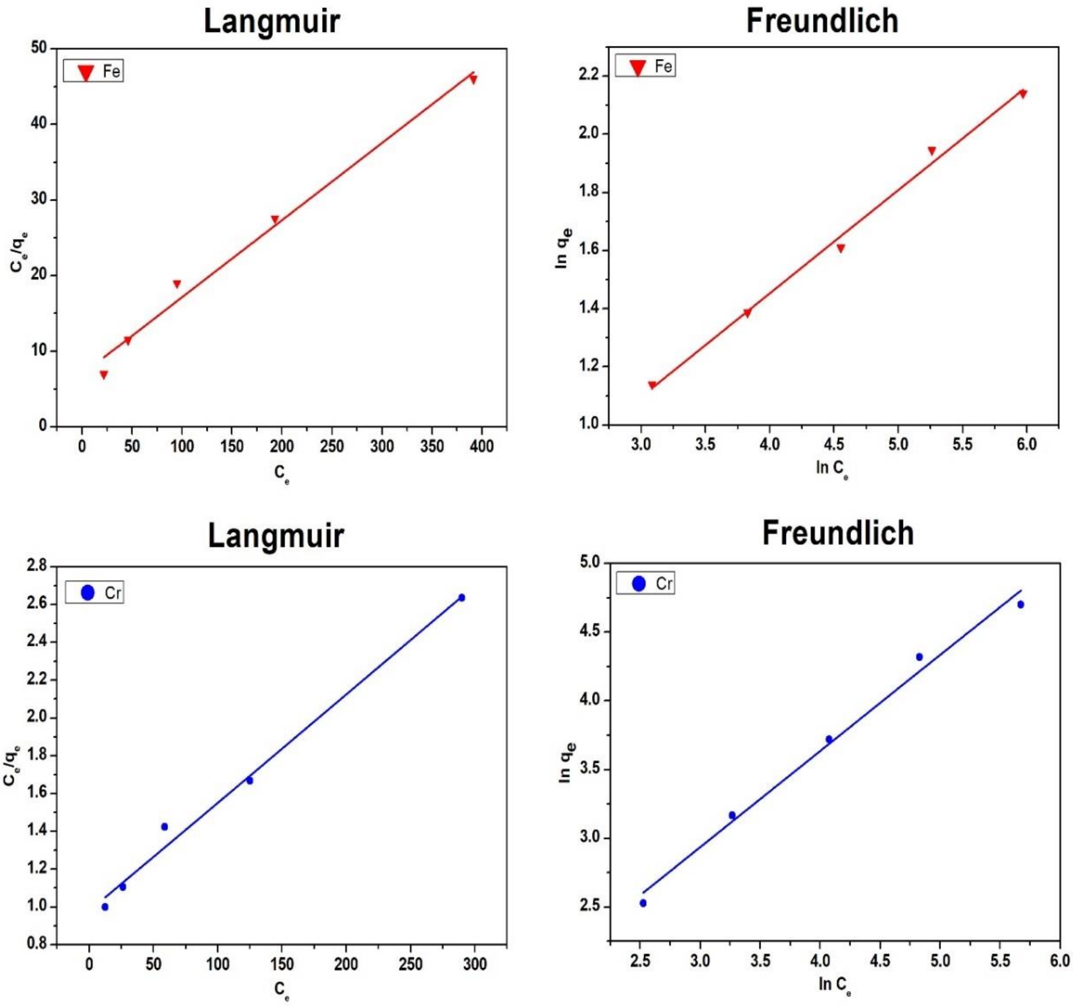


Figure 4.17 Linear plots of Langmuir and Freundlich isotherm models of adsorption of Fe and Cr by cotton-*g*-PEDAMA. Conditions: initial concentration of Cr and Fe ions, 25-400 mgL^{-1}; cotton-*g*-PEDAMA, 1 gL^{-1}; pH 6.0, 25 ^{0}C, 24 h.

Table 4.4. Isotherm co-efficient for adsorption of metals by cotton-*g*-PEDAMA

Metal	**Langmuir**			**Freundlich**		
	q_m	K_l	R^2	K_f	n	R^2
Fe	9.797	0.0146	0.993	1.0310	1.3043	0.995
Cr	174.4	0.0058	0.997	2.3118	1.43	0.994

Freundlich isotherm model usually describes a heterogenous system and the characteristics of adsorption. Following experimental data were investigated for both models and the R^2 values indicates the better fitting of these experimental data to both consecutive models. Important parameters associated with both models tabulated in the Table 4.4 Adsorption of Fe by Cotton-*g*-PEDAMA showed best fitting to Freundlich isotherm model with the R^2 value 0.9997 and adsorption of Cr showed best fitting to Langmuir isotherm model with the R^2 value 0.9994 represented in the Figure. Linearity of these experimental data to both models exhibit the adsorption nature towards Fe and Cr by synthesized Cotton-*g*-PEDAMA adsorbent.

4.5.3 Kinetics studies

Adsorption of Fe and Cr by Cotton-*g*- PEDAMA investigated with kinetics models pseudo first order Eq. (8) and pseudo second order Eq. (9) to evaluate the adsorption efficiency with respect to time.

$$\ln(q_e - q_t) = \ln q_e - k_1 t) \qquad (8)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (9)$$

where qe (mg g^{-1}) and qt (mg g^{-1}) are the mass of adsorbed metal ions per unit mass of the adsorbent at equilibria and time (t), respectively, and k_1 (g mg^{-1} min^{-1})

and k_2 (dm^{-3} mg^{-1} min^{-1}) are the rate constants of pseudo-first-order and pseudo second-order models, respectively.

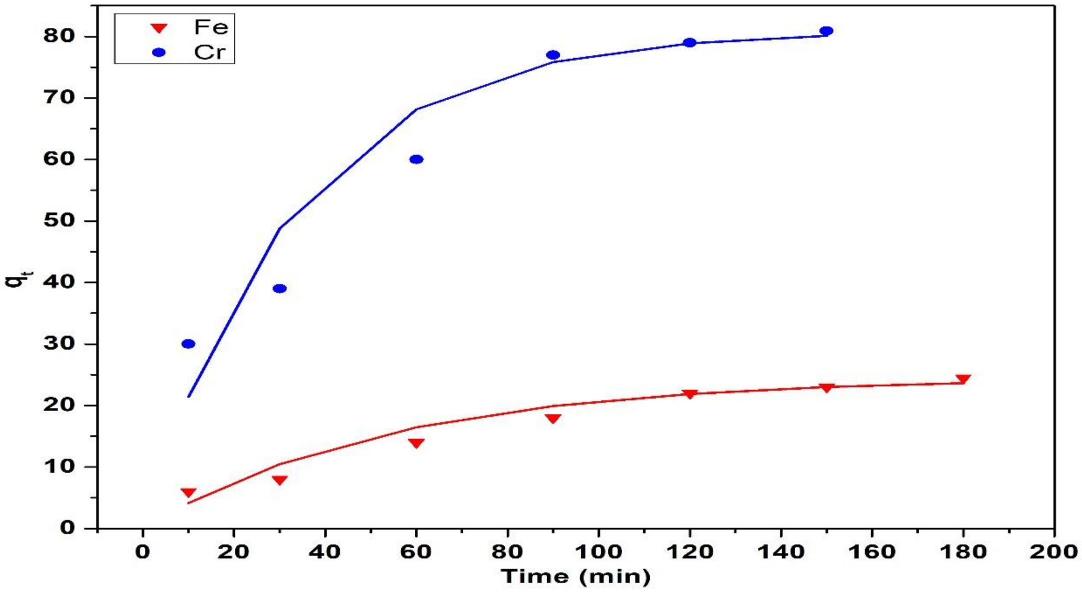


Figure 4.18 Adsorption kinetics of Fe and Cr by cotton-*g*-PEDAMA. Conidtions: initial concentration Cr and Fe, 50 mgL^{-1}; cotton-*g*-PEDAMA,1 gL^{-1}; pH 6.0,25 ^{0}C, pH, 6.

The kinetics model studies interpret with experimental data and exhibit the dynamic characteristics of adsorption of Fe and Cr by Cotton-g-PEDAMA. The metal uptake capacity (qt, mg/g) for the kinetic data calculated using the following eq. 5 and represented in the Figure 4.18

$$q_t = \frac{(C_0 - C_t)v}{m} \qquad (5)$$

where C_t and C_0 are concentrations (mg^{L-1}) at time t and 0 respectively and v represents the solution volume (L), and m is the adsorbents mass.

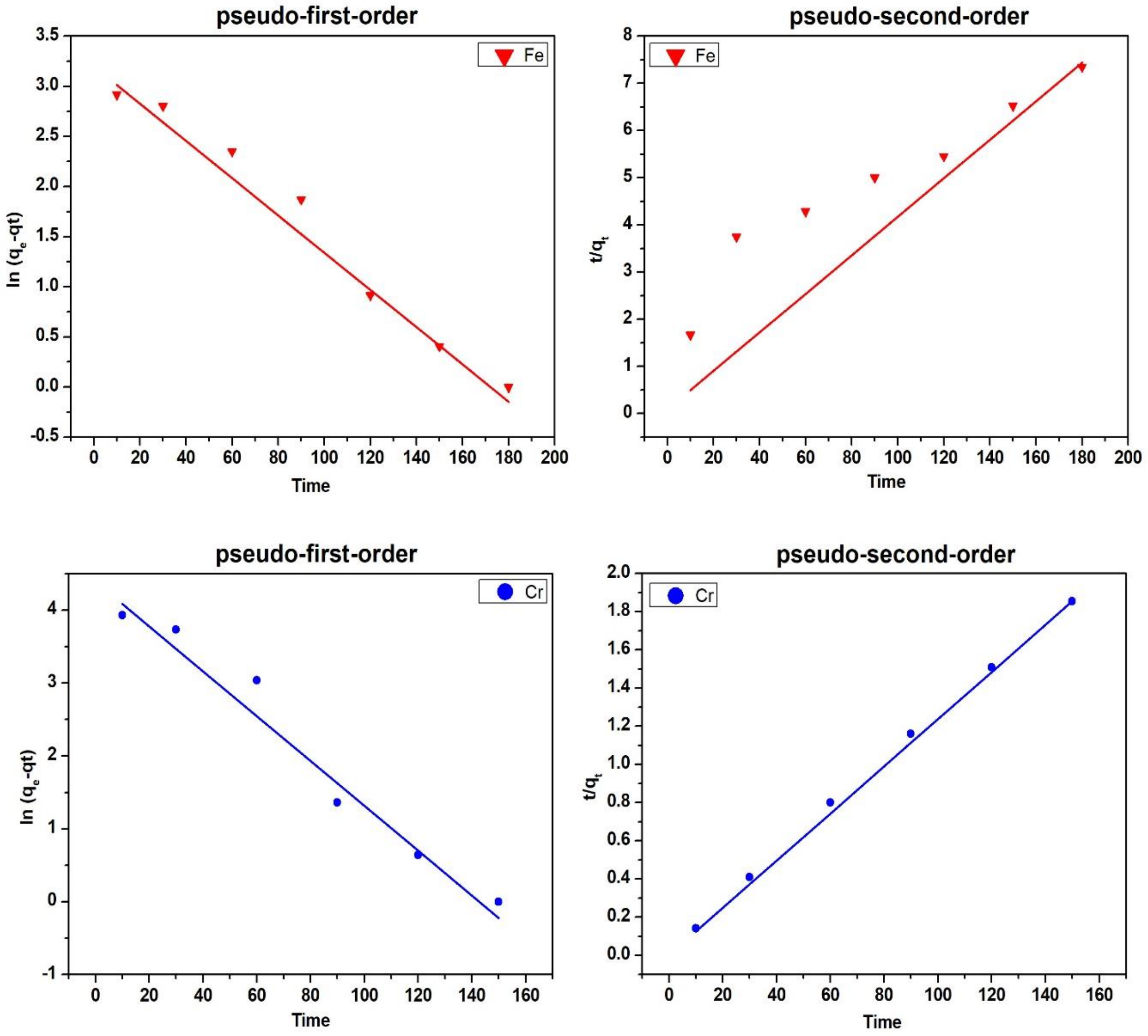


Figure 4.19 Linear plots of pseudo-first order and pseudo-second-order model for adsorption of Fe and Cr by cotton-*g*-PEDAMA. Conditions: initial concentration of Cr and Fe ions, 50 mgL^{-1}; cotton-*g*-PEDAMA, 1 gL^{-1}; pH 6.0, 25 ^{0}C

In the kinetics studies, Figure 19 demonstrate the correlation of experimental data with both kinetics model for adsorption of Fe and Cr, hence adsorption of Fe showed best fitting to pseudo first order model and adsorption of Cr showed best fitting also to pseudo first order model with R^2 values 0.9901 and 0.9900 respectively. The important parameters related with these kinetic models e.g. The rate constants, linear correlation coefficients (R^2), and both experimental (q_e, exp) and calculated (q_e, cal) uptake values for Fe and Cr metals are represented in Table 4.5.

Table 4.5. Kinetics co-efficient for adsorption of metals by cotton-*g*-PEDAMA

Metal	**Pseudo first order**				**Pseudo second order**			
	K_1 (min^{-1})	R^2	qe, cal (mg/g)	qe, exp	K_2 (min^{-1})	R^2	qe, cal (mg/g)	qe, exp
Fe	0.0006	0.9901	26	19.4	0.0191	0.9442	26	25.7
Cr	0.0210	0.9900	51	49.85	0.0298	0.9803	51	50.81

4.5.4 Reusability of Cotton-g-PEDAMA

From the commercial view of point using 3 different desorbing agents the reuse and regeneration investigated according adsorption-desorption capacity of cotton-g-PEDAMA showed in Figure 4.20. This investigation shows that maximum desorption capacity acquired with 0.5M HNO_3 solution for both metals Fe and Cr where other two desorption agents 0.5M NaOH and 0.5M HCl showed lesser efficiency. Maximum desorption efficiency obtained by 0.5M HNO_3 for cotton-g-PEDAMA is about 85% for Fe and 54.5% for Cr adsorption

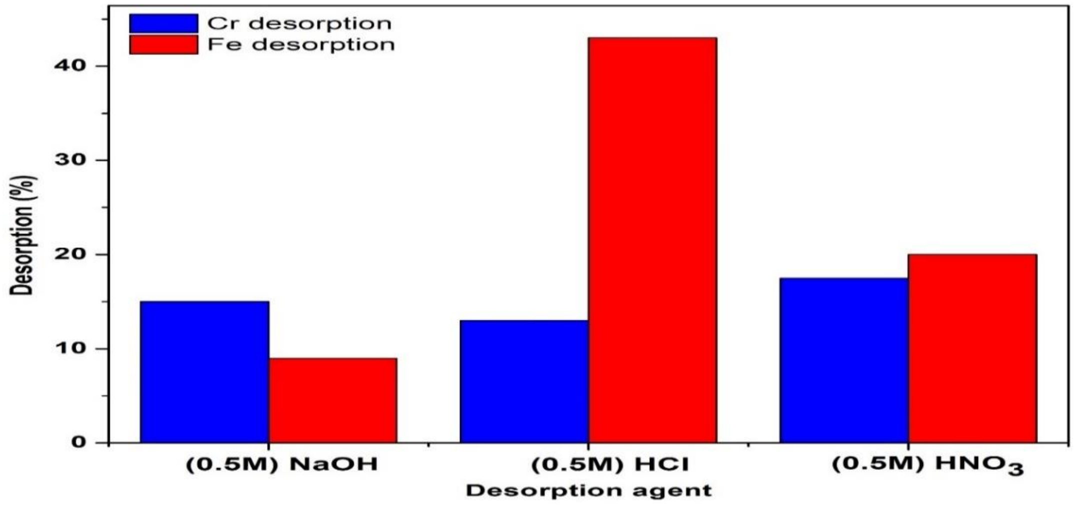


Figure 4.20 Desorption percentage by three desorbing agents 0.5M NaOH, 0.5M HCl and 0.5M HNO_3

To evaluate the reusability characteristics of cotton-g-PEDAMA it also subjected to 5 number of cycles of adsorption and desorption process. Figure 4.21 demonstrate the experimental outcomes of the reusability test as the adsorption capacity of cotton-g-PEDAMA towards Fe and Cr decreased a little from its initial efficiency of adsorption which was 97% for Cr and 84% for Fe. Hence this analysis ensured that synthesized adsorbent conduct good reusability property which makes it more sustainable.

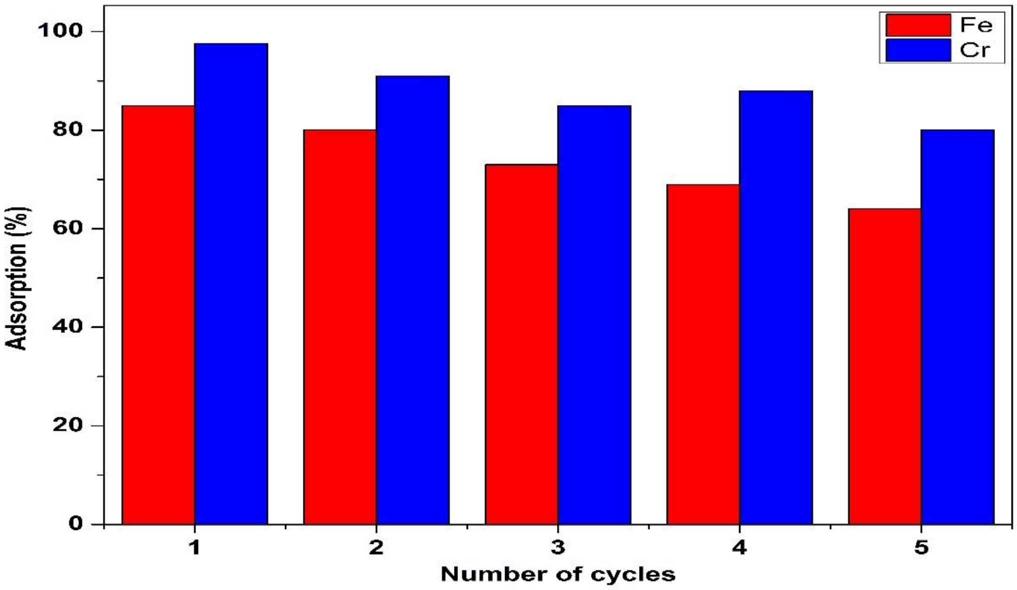


Figure 4.21 Reusability of cotton-g-PEDAMA

4.5.5 Industrial application

Two samples were prepared containing Fe and Cr. Concentration of Fe and Cr was maintained same as reported in the literature. Solutions was prepared that contains Fe and Cr metals. Cotton-g-PEDAMA added into solution to adsorb metals from the solution mixture. Concentration of metal solution determined after the adsorption process and calculated the adsorption efficiency by percentage of adsorption. Adsorbent= 1g/L; 25 °C, 24 hr, pH= 6. Showed good Cr removal efficiency from samples-01 and also sample-02. Which experimental data and graph are represented in the Table 4.6 and Figure 4.22 respectively.

Table 4.6. Adsorption of metals by cotton-*g*-PEDAMA from industrial samples

Absorbent- Cotton-g-PEDAMA					
Sample	Components	Concentration (ppm)	Final concentration (ppm)	Adsorption (ppm)	Adsorption %
1	Fe	20	9.6	10.4	52
	Cr	0.12	0.012	0.108	90
2	Fe	45	27	18	40
	Cr	0.67	0.0335	0.6365	95

Cotton-g-PEPDAMA exhibits good adsorption towards Cr from both samples prepared.

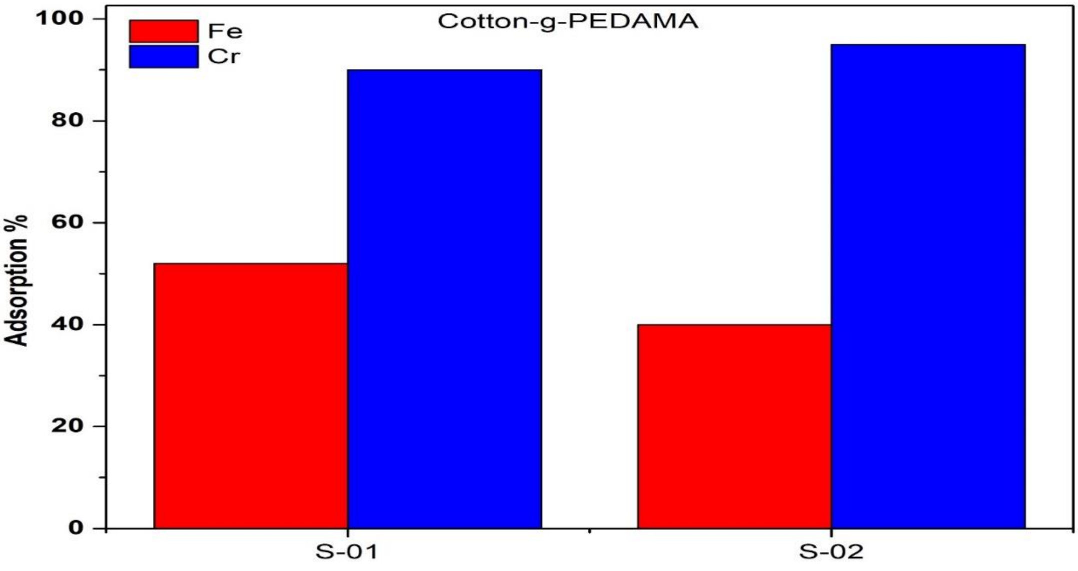


Figure 4.22 Comparative adsorption diagram of Fe and Cr about Sample-01 and Sample-02 for industrial application

Chapter 5: CONCLUSION AND RECOMMENDATION

5.1 CONCLUSIONS

The graft polymerization of a biodegradable metal adsorbent onto cotton for the treatment of industrial wastewater has shown tremendous promise in removing heavy metals, notably iron (Fe) and chromium (Cr). Pure cotton as a substrate for graft polymerization has various benefits, including availability, low cost, and biodegradability. A series of research revealed that the graft polymerization procedure significantly improves the metal adsorption capacities of pure cotton. Cotton fibre functionalization with polymeric grafts increases surface area and chemical reactivity, leading in better metal adsorption effectiveness.

When compared to untreated cotton fibres, the surface area, porosity, and mechanical strength of the synthesized biodegradable metal adsorbent increased significantly. These enhancements contribute to the adsorbent's improved adsorption capability, making it a viable material for the treatment of heavy metal-contaminated industrial wastewater. Batch adsorption tests employing synthetic wastewater samples including Fe and Cr were used to evaluate the efficacy of the biodegradable metal adsorbent. The results showed that both heavy metals were removed with exceptional effectiveness, with Fe and Cr concentrations dramatically dropping following treatment. The adsorbent's adsorption capability was discovered to be affected by a variety of parameters, including pH, starting metal concentration, contact duration, and temperature.

Furthermore, equilibrium and kinetic investigations were conducted to study the adsorption mechanism of Fe and Cr onto the biodegradable metal adsorbent. The Langmuir isotherm model suited the equilibrium data well, indicating monolayer adsorption behaviour. Adsorption kinetics followed a pseudo-second-order model, indicating that chemisorption was the main process. The regeneration and reusability of the biodegradable metal adsorbent were also investigated. The adsorbent demonstrated excellent regeneration potential, preserving its adsorption capability even after many adsorption-desorption cycles. This property improves the adsorbent's economic feasibility and sustainability, giving it a potential alternative to traditional non-biodegradable metal adsorbents.

In final analysis, the graft polymerization of a biodegradable metal adsorbent onto cotton provides a sustainable and effective approach for the treatment of industrial wastewater polluted with heavy metals Fe and Cr. The adsorbent's improved adsorption capacity, high regeneration potential, and biodegradability make it an appealing alternative for industrial applications. More research and optimization are needed to fully realize its potential in large-scale industrial wastewater treatment systems.

5.2 RECOMMENDATIONS OF THIS RESEARCH

In the ever-evolving landscape of environmental science and technology, the synthesis of biodegradable metal adsorbents represents a pioneering avenue for the treatment of industrial effluents. This thesis stands as a testament to the innovative strides taken in this field. However, as we stand at the cusp of progress, it is essential to acknowledge that the journey toward sustainable and efficient industrial wastewater treatment continues. This introduction lays the groundwork for a discourse on the indispensable next steps in research and development, with a focus on enhancing both the theoretical underpinnings and the practical application of the synthesized adsorbent. The recommendations proposed herein emerge as beacons guiding the future trajectory of this research, aiming to address nuances and challenges that remain unexplored in the current thesis. As we delve into the intricacies of these recommendations, we envision a collaborative effort between academia and industry, forging pathways to bridge the gap between laboratory innovations and scalable, real-world solutions. The synthesis of biodegradable metal adsorbents on cotton holds immense promise, not only in terms of pollutant removal but also in aligning industrial practices with environmental sustainability. This discourse on future research recommendations invites a holistic exploration, encompassing aspects such as scalability, long-term efficacy, ecological impact, and practical integration. By heeding these recommendations, we anticipate a nuanced and robust roadmap for further investigations, propelling this research domain toward a future where sustainable industrial effluent treatment becomes an integral part of global environmental stewardship. We recommend the following for future work:

1. Investigating the potential of using different types of metal ions for graft polymerization onto cotton to determine the most effective adsorbent for the treatment of industrial effluent.

2. Exploring the possibility of incorporating other biodegradable materials, such as chitosan or cellulose, into the synthesis process to enhance the adsorption capacity and selectivity of the adsorbent.

3. Conducting a comprehensive study on the regeneration and reusability of the biodegradable metal adsorbent to assess its long-term effectiveness and practicality for industrial applications.

4. Evaluating the performance of the biodegradable metal adsorbent in real industrial wastewater treatment scenarios to validate its efficacy and feasibility for large-scale implementation.

5. Investigating the potential for scaling up the synthesis process of the biodegradable metal adsorbent to meet industrial demand while maintaining cost-effectiveness and environmental sustainability.

6. Exploring potential modifications to improve the mechanical strength and stability of the biodegradable metal adsorbent for prolonged use in harsh industrial environments.

7. Investigating potential applications for spent biodegradable metal adsorbents, such as recycling or repurposing them for other environmental remediation purposes, to ensure a sustainable lifecycle approach.

8. Conducting a comprehensive life cycle assessment (LCA) to evaluate the environmental impact and sustainability of using biodegradable metal adsorbents compared to traditional non-biodegradable alternatives in industrial effluent treatment processes.

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Appendix A:

1. The laboratories of CUFL and BCSIR in Chattogram have the equipment and chemicals needed to measure water and soil quality parameters.
2. This part of the thesis includes essential data.
3. At the time of sampling, some pictures of pollution were taken around the Shipbreaking Yard.

Appendix B: INSTRUMENTS AND CHEMICALS