



# A Critical Review on Natural Fibers Modifications by Graft Copolymerization for Wastewater Treatment

Nur Affah Zubair<sup>1,2</sup> · Rihab MUSAAD Moawia<sup>2</sup> · Mohamed Mahmoud Nasef<sup>1,2</sup> · Martin Hubbe<sup>3</sup> · Masoumeh Zakeri<sup>2</sup>

Accepted: 17 August 2021 / Published online: 26 August 2021

© The Author(s), under exclusive licence to Springer Science+Business Media, LLC, part of Springer Nature 2021

## Abstract

Graft copolymerization is a distinctive approach to modify the inherently cheap natural fibers (NFs) using different initiators to incorporate synthetic polymer side chains allowing development of novel types of hybrid materials. This method has been widely applied to develop a variety of NFs based adsorbents for decontamination of toxic pollutants from the aqueous environment. However, the development of high-performance adsorbents from NFs is steady challenged by the need to preserve the sustainability during graft modifications and applications. This article critically reviews the progress on modifications of NFs by graft copolymerization of polar monomers on NFs using various initiating methods and their applications in wastewater treatment. Particularly, the applications of the grafted NFs in removal of heavy metal ions, synthetic dyes, oil spills and extraction of precious metals from wastewater are elaborated. The critical challenges to the viability and sustainability of NFs-based adsorbents with respect to functionalization by graft copolymerization and environmental impacts are discussed and the future research directions are also outlined.

**Keywords** Natural fibers · Graft copolymerization · Functionalized bio-based adsorbents · Wastewater treatment · Agro-waste utilization

## Abbreviations

AA	Acrylic acid
AAM	Acrylamide
AIBN	Azobisisobutyronitrile
AASO <sub>3</sub> H	2-Acrylamido-2-methylpropane sulfonic acid
AN	Acrylonitrile
AOBDEPAm	Acryloyloxy-1,3-bis
APCA	Aminopolycarboxylic acid
BA	Butyl acrylate
n-BMA	n-Butyl methacrylate
CA	Crotonic acid
CE-Cell	Cyanoethyl cellulose
β-CD	Beta-Cyclodextrin

CIGC	Chemically initiated graft copolymerization
CM-Cell	Chloromethyl cellulose
CPDTA	Cumyl phenyldithioacetate
CPADTB	4-Cyanopentanoic acid dithiobenzoate
CV	Crystal violet
DAOEPAm	Diethyl(acryloyloxyethyl) phosphoramidate
DCPAA	2,4-Dichlorophenoxyacetic acid
DETAPAA	Diethylenetriamine pentaacetic
DETA	Diethylenetriamine
DEAOEP	Diethyl(acryloyloxyethyl)phosphate
DEAOEPn	Diethyl(acryloyloxymethyl)phosphonate
DEMAOEP	Diethyl (methacryloyloxyethyl) phosphate
DMAOMPn	Dimethyl(acryloyloxymethyl)phosphonate
DMAEMA	Dimethylaminoethyl methacrylate
EA	Ethyl acrylate
EB	Electron beam
EDA	Ethylenediamine
EI	Ethyleneimine
EGBAEETAA	Ethylene glycol-bis (2-aminoethylether)-N,N,N',N'-tetra-acetic acid

✉ Mohamed Mahmoud Nasef  
mahmoudeithar@cheme.utm.my

<sup>1</sup> Malaysia-Japan International Institute of Technology, Universiti Teknologi Malaysia, Kuala Lumpur, Malaysia

<sup>2</sup> Advanced Materials Research Group, Center of Hydrogen Energy, Institute of Future Energy, Universiti Teknologi Malaysia, Kuala Lumpur, Malaysia

<sup>3</sup> Department of Forest Biomaterials, North Carolina State University, Raleigh, NC, USA

EMA	Ethyl methacrylate
GY	Grafting yield
HA	Hydroxylamine
HCHPK	Hydroxycyclohexyl phenyl ketone
HEA	2-Hydroxyethyl acrylate
HEMA	2-Hydroxyethyl methacrylate
HEMAPA	2-Hydroxyethyl methacrylate phosphoric acid
IA	Itaconic acid
MA	Methyl acrylate
MAGC	Microwave-assisted graft copolymerization
MAA	<i>N</i> -Methylolacrylamide
MMA	Methyl methacrylate
MAAc	Methacrylic acid
MAN	Maleic anhydride
MAOETMAC	2-(Methacryloyloxy) ethyltrimethylammonium chloride
MBAAm	<i>N,N</i> -Methylene bisacrylamide
MBArAm	<i>N,N'</i> -Methylenebisarylamide
MG	Malachite green
NFs	Natural fibers
NMDG	<i>N</i> -Methyl- <i>D</i> -glucamine
OPPEE	Octylphenoxy-polyethoxyethanol
PTSC	Phenyl thiosemicarbazide
PIGC	Photo-initiated graft copolymerization
PsIGC	Plasma-initiated graft copolymerization
RAFT	Reversible addition—fragmentation chain transfer
RIGC	Radiation-induced graft copolymerization
SSS	Sodium 4-styrenesulfonate
VA	Vinyl acetate
VIm	1-Vinylimidazole
VBTMAC	Vinylbenzyltrimethylammonium chloride

## Introduction

With the increase in global energy demand and ecological risks, natural fibers (NFs) have attracted much interest owing to their potential of serving as alternatives to petrochemical-made fibers. Although the strength of such fibers is lower than the synthetic counterparts, but it is enough for usage in many applications including production of food, fine chemical and green materials of wide applications such as nanocellulose [1]. NFs are defined as substances produced by plants (e.g. flax or cotton) and animals (e.g. cashmere and camel hair), which have the capability to be spun into thread or filaments that can be woven, bound, matted or knitted [2]. They have been used in industries such as paper and textile in addition to their use as raw materials in the construction industry.

Flax, cotton, and silk are the oldest NFs utilized by mankind, whereas coir and jute have also been used for a long time. Plant fibers comprised of cellulose unlike animal fibers which embody proteins. The presence of such compounds endowed several advantages such as low cost, low-density, enhanced toughness, biodegradability, reduced respiratory irritation and acceptable levels of strength [3–5]. The breathability of NFs has been utilized effectively in textiles, contributing to comfort. Wearers of clothing made from NFs also are less prone to allergies or skin rashes that are normally associated with the use of synthetic polymers [2]. In addition, NFs easily take up dyes and form uniform colors, while their lengths and strengths can be adjusted according to the specified requirements. For these reasons, the demand for NFs has continued to rise despite the competition from the synthetic polymers, which are non-degradable and release considerable amounts of carbon dioxide and other forms of waste upon disposal, posing a great environmental challenge.

The use of NFs for removal of pollutants such as heavy metal ions, dyes and oil spills from aqueous media is a field that is receiving extensive research efforts because of their promising applications in biosorption processes [6]. Moreover, NFs are known for their abundance, low cost and structural properties, all of which make them potential biosorbent materials [7]. However, NFs must undergo biological, physical, chemical modifications to improve their characteristics such as the mechanical properties, adhesion, surface tension, strength, porosity, crystallinity, permeability, solubility, and chemical reactivity. Chemical modifications such as mercerization (alkaline treatment), acylation, bleaching and graft copolymerization are commonly used for treatment of NFs. This is not only because of their quick and effective procedures but also due to ability to make permanent changes compared to that of physical methods [8]. Of all methods, graft copolymerization is an interesting technique that has been increasingly used to impart permanent modifications to NFs. This technique involves the introduction of synthetic polymers originated from grafting monomers to NFs leading to the development of various graft copolymers with improved physico-chemical properties without compromising the basic properties of NFs [9]. Particularly, properties such as flexibility, stability, resistance to microbial degradation, hydrophilicity, metal ions binding capacity can be imparted by graft copolymerization. Therefore, functionalized NFs found several important applications including the development of green composites [10, 11] and chelating adsorbents [12, 13].

There have been many reviews covering various aspects of NFs including their types and composition [14–16], chemical treatment methods [17–19], and applications in development of green composites [20–26]. Some reviews were particularly dedicated to modification

of carbohydrate polymers (e.g. starch, cellulose, chitosan, and alginate) with various methods including blending, grafting, combination with different nanomaterials or their nano-cellulosic form and their potential applications for removal of heavy metal ions and synthetic dyes [12, 13] and controlled drug release, battery separators and smart food packaging materials [27]. Other published reviews addressed graft modifications of cellulose using living/controlled polymerization methods [28] and conventional grafting methods of wool fibers [29]. However, most of these articles focused only on reviewing the bright aspects of graft modification methods pertaining to properties and various applications of the modified NFs without addressing neither the preferences for grafting methods nor their environmental impacts and the adherence to green chemistry. Thus, there is a demand to address such missing issues with the focus on the widely investigated graft modified NFs targeting removal of toxic species from wastewater and their preparation by various graft copolymerization methods.

The objective of this article is to provide a critical review for various graft copolymerization methods used for modification of NFs and the progress in the developed grafted adsorbents for the adsorption of toxic pollutants from wastewater taking the methods robustness, environmental impacts and overall sustainability into consideration. The scope of the article covers an overview of NFs and various graft copolymerization techniques for functionalization of NFs by chemical-, photochemical-, radiation-, thermal- and plasma-initiation, together with an evaluation for their merits and demerits. The applications of NFs-based adsorbents for removal of heavy metal ions, dyes, and oils from wastewater together with the extraction of precious/rare earth metals from waste streams are summarized. The challenges to the grafted NFs (adsorbents) sustainability and future research directions are critically discussed.

## Categorization of Natural Fibers

NFs can be categorized based on their origin into basis into plant, animal, and mineral fibers, as shown in Table 1. The latter are naturally occurring fibers such as asbestos, ceramic, and metallic fibers and are beyond the scope of this review. NFs cover a wide spectrum of fibers that ranges from the most dominant and widely used cotton fibers to other specialty fibers such as cashmere that is produced in significantly smaller quantities. NFs from plants can be further classified depending on plant source into: (i) seed fibers, which are collected from seeds or seed cases such as cotton and kapok; (ii) leaf fibers, which are collected from leaves such as sisal and agave; (iii) bast fibers that are collected from skin or baste surrounding the stem such as flax, kenaf, jute, hemp, ramie, rattan, soybean, vine and banana fibers; these fibers are used for making durable yarns, fabrics, papers and packaging, because of having higher tensile strength than other fibers; (iv) fruit fibers, which are collected from the plant fruit such as coconut (coir), and stalk fibers such as straw of wheat, barley, rice and crops like grass and bamboo. More details on different classes of NFs can be found in previous reviews [31].

All plant fibers are incorporating cellulosic structures embodying cellulose, hemicelluloses lignin and assembled in bundles of fibrils with irregular diameters harboring gaps and defects. However, cellulose is the most important component, and its contents control the mechanical properties of the fibers [32]. Compared to synthetic fibers, NFs have inconsistent quality varying from one location to another depending on soil and climate. In general, they have hydrophilic nature prompting the need for modification depending on the application.

Cellulose has a ribbon-like shape, which allow twisting and bending in the direction out of the plane in away imparting moderate flexibility [33]. The presence of the hydroxyl (–OH) groups forms intermolecular hydrogen bonds within

**Table 1** Categorization of natural fibers [23, 30]

Natural fibers	Source	Example
Plant/cellulosic fibers	Bast	Flax, hemp, jute, kenaf, ramie, Mesta and roselle
	Leaf	Abaca, banana, pineapple, sisal and henequen
	Seed	Cotton, kapok, luffa, and milkweed
	Fruit	Coir and palm oil fruit
	Stalk	Rice, wheat, maize, barely, oat and rye
	Wood	Softwood and hardwood
	Grass/reed	Bamboo and bagasse
Animal fibers	Wool	Cashmere, lamb wool, angora wool and alpaca
	Hair	Goat hair, horsehair, and camel hair
	Silk	Mulberry and tussah
Mineral fibers	Minerals	Asbestos, brucite and wollastonite

cellulose molecules and creates moderately strong interactions involving neighboring cellulose molecules in dry fibers. Chemical reactivity of cellulose is largely related to the reactivity of the electron donating –OH groups [33]. Nowadays, the main uses of cellulose are in making paper products or cardboard, membranes, tissue, explosives, textiles, and construction materials. Major efforts have been carried out to chemically modify cellulose to increase its resistance to heat and abrasion [34] mechanical stability [35] and anti-bacterial activity [36].

Animal fibers are the second source of NFs, and such fibers can be classified into: (i) silk fibers, which are collected during the preparation of cocoons from dried saliva of silkworms, and (ii) wool fibers including cashmere, lamb wool, angora wool, alpaca and animal hair such as goat hair, horse hair, camel hair and avian fibers, which originate from birds feathers [37]. Unlike plant counterparts, animal fibers are mainly composed of specific proteins, making each type of fibers have properties differing from each other. The molecular structures of the basic unit of cellulose fibers compared to those of wool and silk fibers are shown in Fig. 1.

Like plant NFs, animal fibers can undergo chemical modified by reactions involving grafting, coupling and amino acids. The modified fibers have potential for applications in composites, antimicrobial materials and adsorbents [29, 38]. On the other hand, the use of mineral fibers such as asbestos was banned due to risk to human health caused by exposure [23]. Thus, this article will focus on the modifications of cellulosic and animal NFs for imparting ionic characters by graft copolymerization.

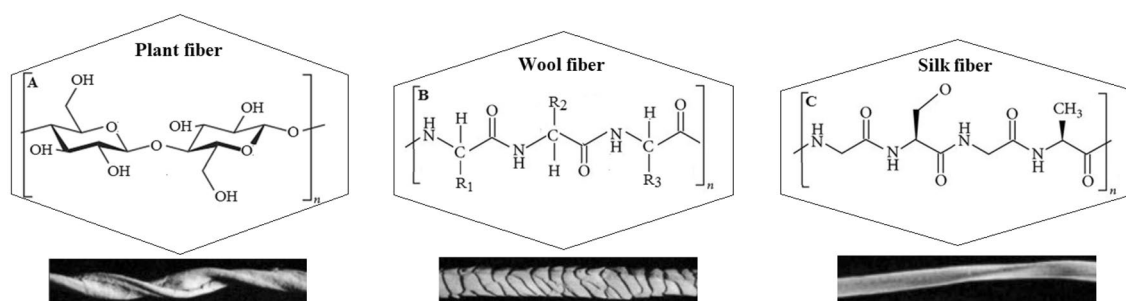
## Treatments for Natural Fibers

To improve the NFs properties and make them suitable for target applications, various chemical, biological, mechanical methods or their combination and physical modification are known [39]. However, the two main treatments that are usually used are physical and chemical methods. The former extends some changes to the surface and morphological

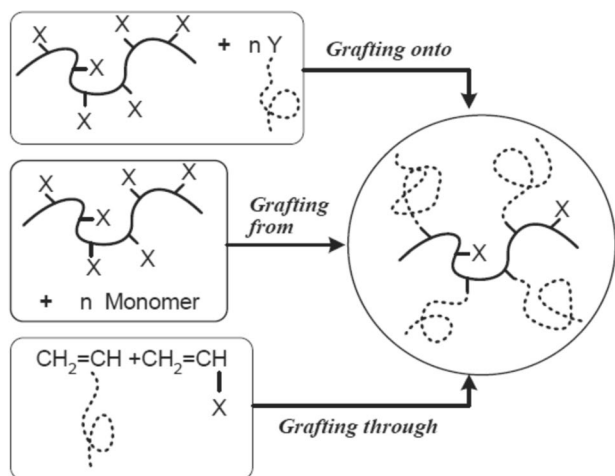
properties of the fibers without changing their chemical composition. Physical treatment includes processes such as stretching, calendaring, rolling, swaging and thermal treatments in addition to the use of different rays, plasma, or steam explosion. Unlike physical methods, the chemical treatments introduce chemical changes such as activation of hydroxyl groups, imparting new moieties that can effectively interlock with matrices using silane as coupling agents and chemical coupling (acylation or esterification). Several chemical treatments are commonly used for surface modification of NFs including mercerization, acetylation, cyanoethylation, benzoylation, isocyanates treatment, dewaxing, esterification, etherification treatment and graft copolymerization [40]. Such treatments not only improve the NFs wettability and adhesion with the polymer matrices but also impart unique properties and functional group as well as facilitate processing. More details on the chemical treatment of NFs can be found in a few reviews that have been published [37–41].

## Graft Copolymerization onto Natural Fibers

Graft copolymerization is a reaction that leads to formation of graft copolymers in which several side chains are covalently attached to a linear backbone. The resulting copolymer has new characteristics originated from two or more parent polymers. In the present context, the definition is broadened to emphasize the attachment of the side chains to a cellulosic surface. At a commercial level, the most significant copolymers are derived from the vinyl monomers such as ethylene, styrene, vinyl chloride and acrylonitrile. The sequence of the monomer units varies depending on the distinct reactivity of the monomers during the polymerization process and reaction parameters. Three approaches are usually adopted to synthesis graft copolymers as depicted in Fig. 2. The first one is “Grafting onto” and it includes the reaction of a reactive group on a macromolecular chain with a second polymer. The second approach is “Grafting from” and it involves a polymerization reaction between a



**Fig. 1** Molecular structures of basic unit of: **A** plant, **B** wool and **C** silk fibers

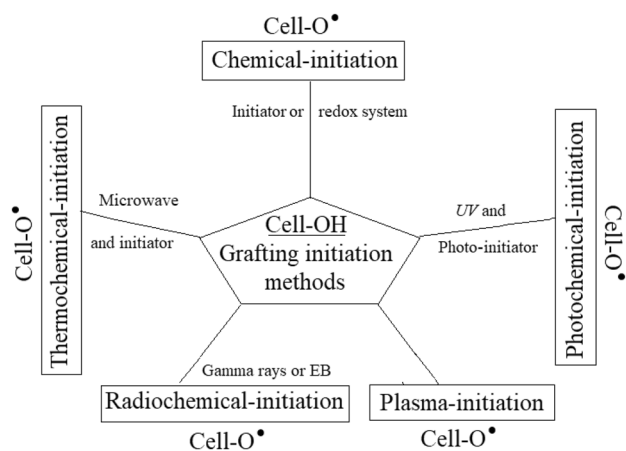


**Fig. 2** Schematic representation of approaches for preparation of graft copolymers [42]

polymer with functional groups (macro-initiator) with a succession of monomers, which build a side chain. “Grafting through” is the third approach and it includes polymerization of macromonomer(s) [42]. Modifications of NFs by graft copolymerization commonly follow “grafting from” approach, and many studies have applied this technique for preparation of a variety of graft copolymers based on NFs.

Graft polymerization is a method that is used to alter properties of substrates such as NFs to meet the requirements of specific applications. The altered properties include elasticity improvement, bending strength, fastness, solubility, moisture absorption, thermal resistance and reactivity. The level of changes in such properties is dependent on the conditions of the reaction. Graft copolymerization of NFs usually proceeds by the free radical mechanism that is initiated by one of 5 different initiation routes (as shown in Fig. 3): (i) chemical initiation, (ii) thermal initiation which is assisted by microwave, (iii) photo-initiation with *UV* light in presence of photo-initiator, (iv) plasma-initiation and (v) radiation- (radiochemical-) initiation using high energy radiation [43].

The presence of these initiators generates free radicals on the parent cellulose backbone (mostly after delignification with a chemical treatment) which form macroradicals when reacted with a monomer, which propagate to become graft growing chains that form graft copolymers after termination [44]. Monomers to be grafted can be either vinylic or acrylic monomers and grafting reaction may involve one monomer or a mixture of at least 2 monomers [41]. Figure 4 shows a list of common monomers that have been used for modification of NFs by graft copolymerization. The widely used polar monomers for modification of NFs include but not limited to acrylic acid (AA) glycidyl methacrylate (GMA), acrylonitrile (AN), and methyl methacrylate (MMA). The



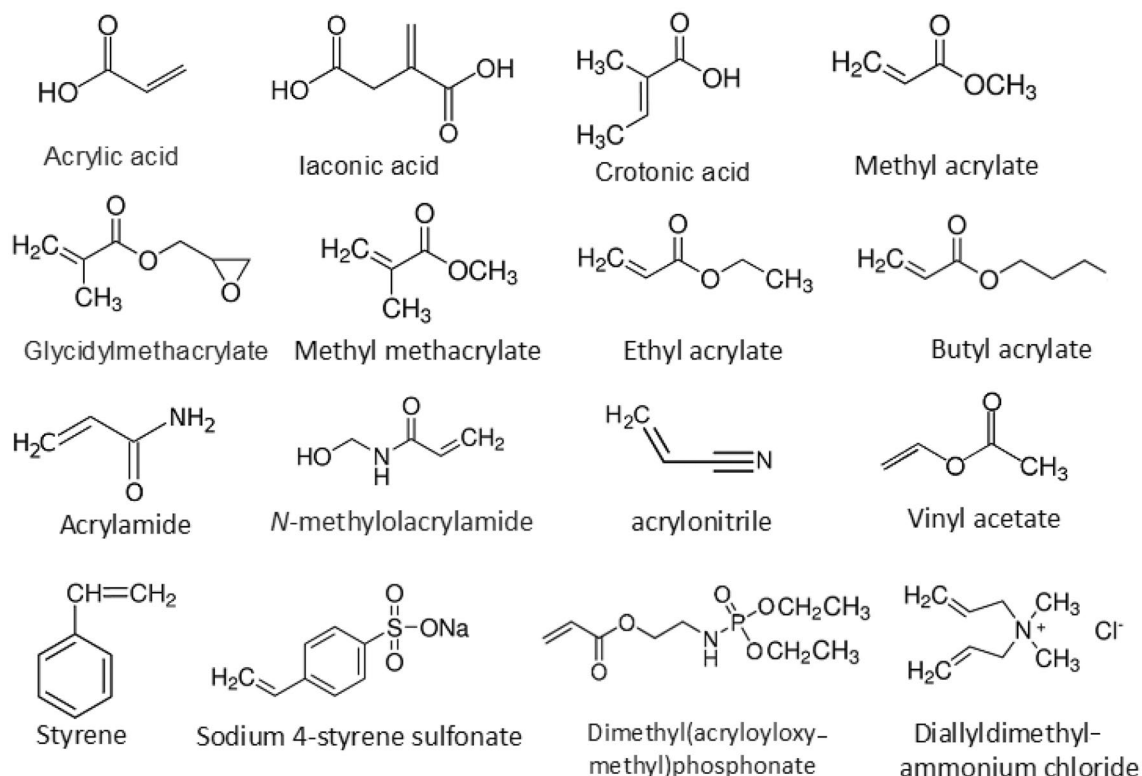
**Fig. 3** Schematic diagram of various graft copolymerization initiation techniques for modification of NFs

polarity of such monomers imparts desired functional groups to the cellulose backbone while maintaining its properties [8]. Similarly, wool fibers can be treated with graft copolymerization techniques using different monomers to impart desired surface properties. A review on grafting of various monomers into wool under different combinations of reaction parameters and the properties of the grafted wool fibers together with their potential applications was reported by Shavandi and Ali [29]. More details on the various methods for initiating graft copolymerization of NFs are discussed in the next sections.

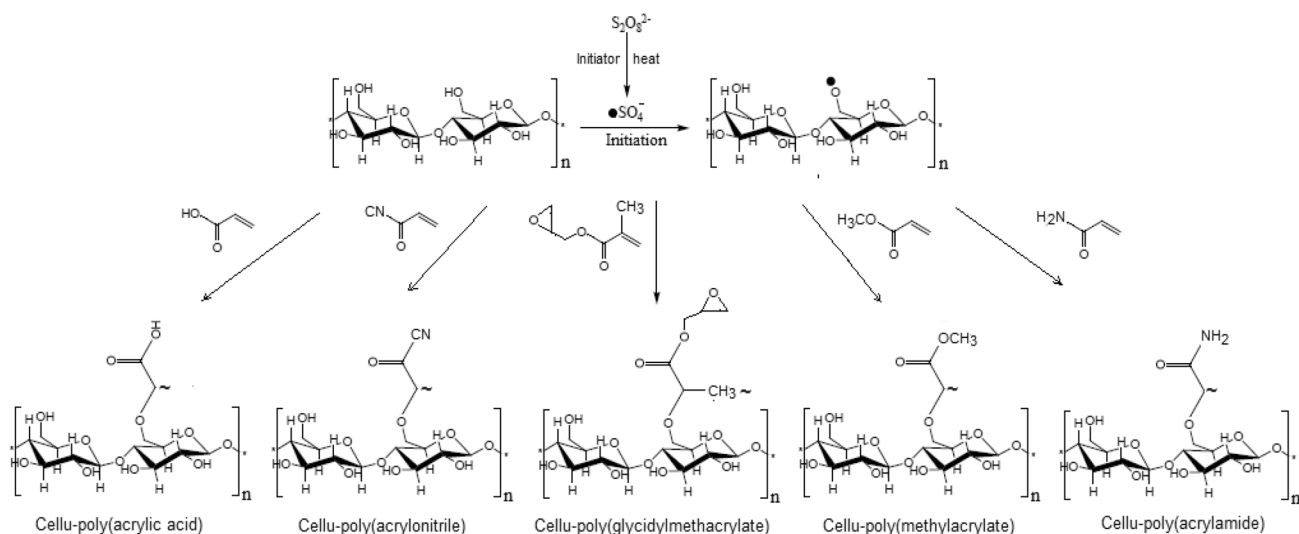
## Chemically-initiated Graft Copolymerization

In chemically-initiated graft copolymerization (CIGC), radicals are initiated in cellulosic fibers by free radical-producing initiators or redox systems such as ceric ions: ceric ammonium nitrate [45], cerium sulphate [46], ceric ammonium sulphate [47], ferrous iron-hydrogen peroxide ( $\text{Fe}^{2+}-\text{H}_2\text{O}_2$ ) [48], cobalt (III) acetylacetonate complex salts [49] and manganese (III)/sulfuric acid [45]. Alternatively, free radical generators such as azobisisobutyronitrile (AIBN) [50], potassium persulfate ( $\text{K}_2\text{S}_2\text{O}_8$ ) [51], ammonium persulfate [ $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ] and benzoyl peroxide ( $\text{C}_{14}\text{H}_{10}\text{O}_4$ ) [52] have been also used. It is well established that the type of initiator and monomer have important effects on the grafting level. A schematic representation for preparation of various graft copolymers by chemical initiation and reaction with different monomers is shown in Fig. 5.

A significant amount of work has been conducted using CIGC of different monomers onto various NFs. For example, itaconic acid (IA) was grafted onto sisal fibers using potassium persulfate as an initiator under different reaction conditions [53, 54]. The grafting yield (GY) [55] was found



**Fig. 4** List of monomers commonly used for modification of NFs by graft copolymerization



**Fig. 5** Schematic representation for preparation of various graft copolymers by chemical initiation and reaction with different monomers

to be a function of reaction conditions such as the concentrations of IA and the initiator. Earlier Mishra et al. [56] grafted AN onto sisal fibers using  $NaIO_4$  and  $CuSO_4$  as initiators. The study concluded that both GY and the fibers' properties were depended on the reaction conditions (concentrations of the initiator and monomer and reaction time). In another

study, Pulat and Isakoca [57] grafted various monomers with carboxylic acid groups such as AA, crotonic acid (CA), and IA onto cotton fibers using benzoyl peroxide as an initiator. Maximum GY of 23.9% was reached after optimization of reaction conditions.

CIGC of methyl acrylate (MA) and MMA onto jute fibers using a redox system composed of potassium persulfate (initiator) and ferrous sulphate (catalyst) was investigated in various occasions [11, 58, 59]. Variation of reaction conditions including monomer concentration, initiator concentration, catalyst concentration, reaction time and temperature was used to control GY, which reached a range of 17–20% upon optimization. The properties of the grafted fibers such as dye absorption, tenacity, color fastness was favorably altered. Jute fibers were also grafted with other acrylate monomers such as ethyl acrylate (EA) and 2-hydroxy ethyl methacrylate (HEMA) using the same redox system under optimum conditions [60]. Grafting brought about an improved strength, a higher thermal stability, and a surface smoothness to the grafted jute compared to pristine counterpart. Furthermore, the reactivity of lignocellulosic jute fibers to sunlight [60], atmospheric gases and chemicals was enhanced by the grafting [61].

Sharma and Sunil [62] used ceric ammonium nitrate as redox initiator to graft a mixture of MMA with butyl acrylate (BA) or EA was grafted on mulberry silk fibers in an aqueous medium under different reaction conditions. The grafted fibers acquired improvements in the thermal resistance, moisture absorbance and chemical stability.

In summary, it can be stated that CIGC can effectively modify the NFs and enhance their adsorption properties. However, one of the main concerns about the use of CIGC techniques is the need to extract the grafted fibers from the homopolymer without destroying their structure. Moreover, the discharge/residue from the solvent extraction process containing impurities (catalyst, initiator, solvent and homopolymer) is harmful to the ecosystem and causes serious environmental pollution. This poses a

critical challenge to CIGC method and promotes the use of alternative greener grafting methods.

## Radiation-initiated Graft Copolymerization

RIGC is an appealing method for conferring new properties originated from polar monomers into polymer substrates such as NFs without altering their inherent properties using high-energy (ionizing) radiation. This method permits a desired control over GY, which is a function of grafting parameters in addition to maintaining the purity of the product due to the absence of detrimental impurities [63]. RIGC can be carried out by high energy sources such as Co-60 and electron beam (EB) accelerators. The former produces  $\gamma$ -rays, which have the advantage of deep penetration in the substrates allowing a wide range of GYs during grafting depending mainly on the absorbed dose and dose rate, which decrease continuously with the source decay. Thus, irradiation to certain dose takes longer time (few hours) with the decrease in the dose rate. On the other hand, EB has the advantage of short irradiation time (a few minutes) and high as well as controlled dose rate. However, the penetration depth EB depends on the acceleration energy of electrons and the density of the irradiated substrate [44]. A comparison between  $\gamma$ -rays and EB together with other low energy radiations used for graft copolymerization is presented in Table 2. Unlike microwave, plasma and photo-initiated grafting, RIGC is capable of achieving bulk modifications and has been extensively investigated for preparation of various ionic and chelating polymers [64]. From practical point of view, EB is more advantages for grafting initiation on NFs, which can be achieved not only in a few minutes with GY varying from surface to bulk but also in a more convenient

**Table 2** Comparison between various high-energy and low-energy radiation types

Radiation energy	Radiation type	Sources	Merits	Demerits
High energy	$\gamma$ -rays	Co-60 or Ce-137	High penetration levels, low temperature, leaves no detrimental residue and dose rate can be controlled	Induce structural damage, dose rate is lower than EB, takes relatively long time to reach desired dose and dose rate keep decreasing with natural decay of Co-60
	EB	Accelerators	Fast, low temperature, easy to control, leaves no detrimental residue and high dose rate	Induce structural damage, generated by EB accelerator requiring higher capital investment and low penetration in dense thick materials
Low energy	UV	UV lamp	Low temperature, cheap and leaves no residue	Low penetration and long time
	Plasma	Plasma reactor	Low temperature, fast and create surface changes	Low penetration commences variation in physical and chemical properties and leaves reactive species
	Microwave	Microwave source	High temperature, fast and can also initiate reaction without initiator	Low penetration, establishes physical and chemical property alterations and not recognized by non-polar materials

manner for pre-irradiation method and large-scale applications. Figure 6 shows a typical surface and bulk grafting of polystyrene in flax fibers obtained by RIGC of styrene onto delignified and EB irradiated flax fibers.

When ionizing radiation interacts with NFs, active species are formed, including radicals, which eventually leads to formation of macrocellulosic radicals through abstraction of hydrogen and hydroxyl. Such radicals are responsible for reaction with monomer molecules that initial formation side chain grafts. RIGC techniques can be generally classified into two types: simultaneous irradiation grafting and preirradiation grafting [44]. The former method involves exposing the monomer and the substrate to ionizing radiation at low dose together with addition of a small amount of an inhibitor ( $\text{Fe}^{2+}$  or  $\text{Cu}^{2+}$ ) to minimize the homopolymerization. In the latter method, the substrate is irradiated first and subsequently exposed to the monomer under either inert atmosphere to form trapped radicals or in oxygen to favor formation of hydroperoxyl radicals, where graft copolymerization is subsequently initiated by the thermal decomposition of the formed trapped radicals.

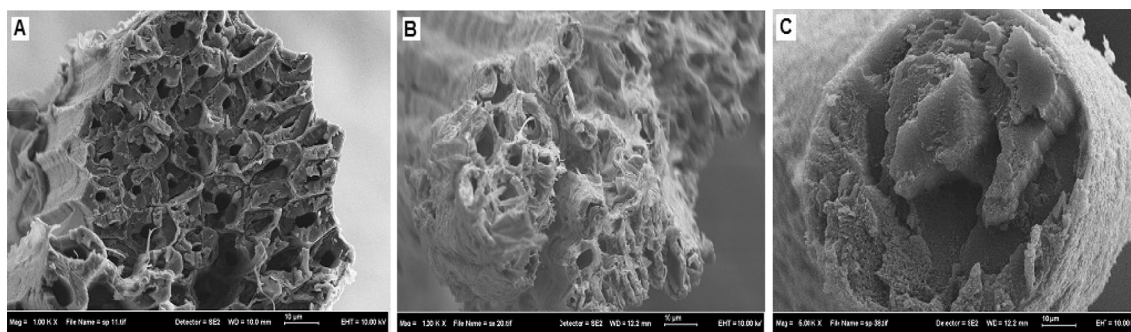
Monomers can be grafted from different phases i.e., vapor, liquid or solid. Moreover, liquid monomers can be grafted while in a neat, a solvent-diluted, or an emulsion mediated form. It is note worthy mentioning that irradiation of polymer substrates induces chain scission and crosslinking in addition to radicals generation allowing grafting to take place in presence of monomers [66]. However, chain scission is likely to dominate the radiolysis of NFs, depending on the level of absorbed dose and dose rate. Thus, the use of high energy radiation methods must be carried out under well-controlled conditions to avoid or minimize the undesired degradation reactions [67].

RIGC is commonly used to modify NFs such as jute and flax fibers by grafting of polar monomers to improve the fibers' compatibility and adhesion during formation of biocomposites [68]. However, imparting ionic groups to NFs by RIGC has received less attention compared to CIGC

method. Cotton printed cloth and cotton mixed fabrics were modified by RIGC of vinyl phosphonate oligomer and *N*-methylolacrylamide (MAA) [28]. The monomer was diluted with water and the reaction conditions were manipulated. The grafted cotton fabrics showed flame retardance without compromising their mechanical properties compared to the untreated fabrics. Cotton fabric was also modified with *N*-phenylmaleimide and *N*-p-hydroxyphenyl maleimide by RIGC to enhance its dyeability as reported by Moktar et al. [69].

Khan [70] grafted jute fibers by RIGC of MMA in an emulsion medium containing octylphenoxy-polyethoxyethanol (OPPEE) using the preirradiation method to improve their properties. A GY of 73% was achieved with dose variation in air compared to 53% in  $\text{N}_2$  atmosphere. The incorporation of poly(MMA) improved the thermal and mechanical properties of the jute fibers compared to the pristine one. In a relevant study, delignified kenaf fibers were also modified by RIGC of GMA [71]. A maximum GY of 150% was achieved at an absorbed dose of 50 kGy. Similarly, delignified flax fibers used RIGC to modify delignified flax fibers by grafting of GMA in an emulsion medium as reported by Moawia et al. [65]. Interestingly, a maximum GY as high as 148% was obtained with samples preirradiated to 20 kGy by EB and reacted with 5% GMA diluted with water in presence of 0.5% surfactant (Tween 20) at 40 °C for 1 h. The use of this green grafting method significantly reduced the amount of monomer, absorbed dose, and made the overall grafting process viable and sustainable. Wool fibers were also modified by RIGC of AA with  $\gamma$ -radiation [72]. The grafted wool fibers gained better tensile strength and elongation % at break compared to the pristine fibers and such improvements increased with higher GY. Moreover, the increase in GY imparted a modest reduction in moisture sorption of the fibers.

Living radical polymerization methods such as reversible addition-fragmentation chain transfer (RAFT) was also used to modify NFs with grafts having controlled molecular



**Fig. 6** SEM images of cross-sections of **A** pristine flax fiber and poly(GMA) grafted flax fibers with graft chains located, **B** at the surface and **C** in the bulk of the fiber [65]



weights. Monomers such as styrene grafted from cellulose by means of RAFT, for which cumyl phenyldithioacetate (CPDTA) was used as a chain transfer agent [60]. RAFT was also used to graft sodium 4-styrenesulfonate (SSS) onto cellulose with 4-cyanopentanoic acid dithiobenzoate (CPADTB) as a transfer agent. The GY was far better than thermal induced grafting of the same monomer onto cellulose [73]. The progress in modification of cellulose using living/controlled radical polymerization (including RAFT) to develop materials with defined structures and adjusted properties were reviewed elsewhere [74].

Although RAFT allows control over the molecular weight and polydispersity index of the grafted chains in NFs, it is rather complicated and requires the use of a RAFT agent. The complexity of RAFT becomes obvious when such technique is integrated with RIGC, leading to a reaction cost escalation. Thus, RAFT seems to be a rather fancy method to modify cheap NFs. It can be concluded that RIGC applying preirradiation with EB in an emulsion medium is the best graft copolymerization technique to reduce the environmental concerns and achieve desired grafting levels in NFs at low doses and minimal monomer consumption without compromising their chemical and mechanical integrity. Moreover, grafting of functional monomers such as AA and SSS in a single step also helps to preserve the mechanical properties of the grafted NFs by avoiding post-grafting functionalization reactions.

## Microwave-assisted Graft Copolymerization

Microwave-assisted graft copolymerization (MAGC) is highly attractive green method with respect to cost effectiveness, time, and environmental friendliness. The exposure of NFs to microwave radiation produces various active species by an additional external redox initiator, which helps to convert the microwave energy to heat that generates free radicals [75]. This method differs from the lesser known counterpart (i.e. microwave-initiated grafting) involving the direct use of microwave radiation in the absence of any free radical initiator to modify NFs, which produces lower GY [76]. The MAGC has the advantage of triggering an immediate processing of reactants in a homogenous manner. The microwave system transfers energy to the reaction bulk in a way enhancing the kinetics of the reaction and increasing the product yield [77]. The application of microwave irradiation for various modifications of polysaccharides by graft copolymerization with and without initiators was reviewed elsewhere [76, 78].

MAGC is frequently used to impart super-water absorbance properties to NFs. For example, cellulose was converted to super-adsorbent by grafting of AA and AAm in presence of potassium persulfate/sodium thiosulfate

initiator and *N,N*-methylene bisacrylamide (MBAAm) cross-linker. A water absorption capacity of 1200 g/g was achieved at 55 °C [79]. The GY could be controlled by manipulation of reaction parameters. For instance, a 70% GY was achieved at AA/cellulose ratio of 14:1, 0.25 wt% initiator to AA and 0.25 wt% crosslinking agent [80]. In another study, Feng and Wang grafted flax shives with AA using microwave irradiation in presence of potassium persulfate as an initiator and *N,N'*-methylenebisarylamide (MBArAm) and a cross-linker [81]. The work yielded an effective superabsorbent resin with rapid water absorbance of 1000 g/g at 7.3 pH.

Grafting of binary mixtures of monomers such as MMA with either ethyl methacrylate (EMA) or EA were carried out on delignified Bhimal (*Grewia optiva*) fibers using microwave irradiation in presence of an initiator composed of ascorbic acid/H<sub>2</sub>O<sub>2</sub> [82]. The reaction parameters including a comonomer concentration were optimized, and the grafted fibers with EA comonomer showed a higher GY mounting to 86.30%. The physico-chemical properties of the grafted fibers showed low swelling behavior, high thermal stability and more chemical resistance compared to other graft copolymers and original fibers. Similar, ascorbic acid/H<sub>2</sub>O<sub>2</sub> initiator was used for grafting of MMA onto *Abelmoschus esculentus* fibers and the reaction kinetics were established [83].

MAGC was also used to improve NFs adhesion properties for composite applications. MMA was grafted onto flax fibers using microwave irradiation as reported by Kaith and Kalia [84]. Particularly, a GY of 24.6% was obtained under microwave of 210 W power. The same fibers were also grafted with binary monomers mixtures such as MMA/vinyl acetate (VA), MMA/AAm, and MMA/styrene using microwave radiations to impart hydrophobicity. The modified fibers with a GY of 24.64% demonstrated a good moisture retardancy and a better tensile strength qualifying them for re-enforcement application than pristine flax fibers [85].

MAGC was also used for surface modification of NFs to conceive better swelling, water uptake, moisture absorbance, chemical resistance, and thermal properties. Particularly, MMA was used to modify century plant (*Agave Americana*) fibers using microwave irradiation in the presence of ceric ammonium nitrate as redox initiator. The GY depended heavily on the reaction conditions, and a maximum GY of 10.4% was achieved [86]. MAGC can be used to improve the surface properties *Bombyxmori* silk fibers properties by grafting with MMA and AN [87]. The modified fibers demonstrated better thermal and chemical stability compared to the pristine one. MAGC was also used to impart ligand for drug delivery without initiator by grafting AA/AN binary mixture onto psyllium [88]. In conclusion, the use of microwave to assist the modification of NFs not only promotes less monomer consumption, higher conversion, and yield

purity, but also it reduces the product cost and encourage green process compared to CIGC.

### Photo-initiated Graft Copolymerization

Photo-initiated graft copolymerization (PIGC) with UV light is a simplified technique that allow surface modification of NFs for better physico-mechanical properties. When UV light falls on a polymer, active species involving radicals, cations or rarely anions are formed. Of all species, radicals are the most active species; they get involved in radical polymerization reactions that take place in the presence of a photo-initiator such as benzophenone and 1-hydroxycyclohexyl phenyl ketone (HCHPK). Several types of photo-initiators have been used and the details of their classification were outlines elsewhere [89].

Monomers such as MMA was grafted onto bleached jute fibers in the presence of  $\text{Fe}_2(\text{SO}_4)_3$  as an initiator under visible light [90]. The optimum reaction conditions were established. A high grafting efficiency and monomer conversion of 80% were achieved in a time range of 2–3 h. To enhance the hydrophilicity of jute fibers, Khan [91] investigated PIGC of methacrylic acid (MAAc) in presence of HCHPK as a photo-initiator. The grafted fibers showed variation in the mechanical and thermal properties with a maximum of a 42% rise in the hydrophilicity compared to pristine jute fibers. The mechanical and electrical properties of jute fabric were also enhanced by PIGC with 2-hydroxyethyl acrylate (HEA) and aliphatic urethane diacrylate oligomer using Darocur-1116 as a photo-initiator [92]. The highest GY was achieved at 73% HEA, 25% aliphatic urethane diacrylate oligomer and 2% Darocur-1116 in 1-min soaking time. The dielectric constant and dielectric loss tangent were improved compared to counterparts of original jute fabric.

Kianfar et al. [93] used PIGC to impart pH sensing properties to cotton fabric for the smart textile application. This was carried out by grafting of Nitrazine yellow (halochromic) modified GMA onto cotton fabric using UV irradiation in presence of benzophenone as an initiator. It can be concluded that PIGC is a suitable method to impart new ionic characters to NFs. However, this method yields low grafting levels, and the grafting is confined to surfaces. Moreover, it takes a long-treatment time to achieve such a little grafting and requires a photo-initiator to start the reaction. Thus, this method is more suitable for surface modification that can help improve the mechanical properties and adhesion between the fibers and polymer matrix giving them more advantage in composite development.

### Plasma-initiated Graft Copolymerization

Plasma-initiated graft copolymerization (PsIGC) is another technique that has been used to modify NFs. Plasma can be defined as a gaseous environment composed of a mixture of active species such as free radicals, electrons and heavy particles in addition to neutral species, making it a unique and diverse media for surface modification of NFs [94]. When plasma interacts with NFs in the presence of a monomer, both gain energy through inelastic collisions of active species and get activated. This initiates graft copolymerization, which takes place either by radicals generated on NFs surfaces followed by contact with a monomer or direct grafting of NFs with activated monomers. PsIGC requires the use of polymerizing gases and monomer precursors such as fluorocarbons, hydrocarbons and silicon ones [95]. The use of plasma techniques provides several advantages over CIGC, including the availability of a large range of monomers, controllability over the level of grafting and fiber damage minimization in addition of being a green technique [96, 97].

PsIGC has been used to improve some mechanical properties of NFs. Zubaidi and Hirotsu [98] modified cotton fibers by PsIGC of HEMA under various conditions (plasma gas source, exposing time of glow discharge, grafting time and temperature). The GY was found to be dependent on the investigated parameters and grafting imparted an improvement in the breaking strength of the modified fibers. On the other hand, PsIGC was used to confer flame retardancy to NFs. For example, Tsafack and Levalois-Grützmacher [99] used Ar plasma for grafting fire-retardant monomers such as, diethyl(acryloyloxyethyl) phosphate (DEAOEP), diethyl (methacryloyloxyethyl) phosphate (DEMAOEP), diethyl(acryloyloxymethyl)phosphonate (DEAOEPn) and dimethyl(acryloyloxymethyl) phosphonate (DMAOMP) to introduce flame retardancy characteristics to cotton fibers. Two other phosphoramidate monomers including diethyl(acryloyloxyethyl) phosphoramidate (DAOEPAm) and acryloyloxy-1,3-bis(diethylphosphoramidate) propane (AOBDEPAmP) were also grafted, and the properties of the obtained modified cotton fibers with all monomers were compared. The cotton fibers modified with AOBDEPAmP showed a synergistic enhancement in the flame retardancy. The flame retardancy of silk fibers was also improved by PsIGC of a phosphorus-based flame-retardant agent onto silk fabric. The obtained silk fabric conceived durable flame-retardant property [100].

PsIGC was also used to introduce a self-detoxification capability a 50/50 nylon-cotton blend by grafting of diallyldimethylammonium chloride (DADMAC) using an atmospheric pressure glow discharge plasma [101]. The

reaction proceeded by free radical chain polymerization, and the modified fabric attained a durable antimicrobial property. Helmy et al. [102] applied PsIGC to graft DAD-MAC on cotton fibers to impart cationic character and enhance the acid dyeability. Various plasma treatment conditions were also applied together with different acid dyes. The dye uptake into the fibers was significantly improved and the need for effluent treatment was reduced.

Despite the advantages offered by PsIGC, the plasma treatment causes degradation and changes on NFs surfaces because of the etching mechanism that generates pits on the fibers' surface area. Moreover, the modifications that can be introduced to NFs are confined to top surface layers and limited to the type of the gases used. Hence, PsIGC fits more development of bio-composites and is less likely suitable for conferring chelation characters for NFs. The advantages and disadvantages of various graft copolymerization methods used for modification of NFs are summarized in Table 3. It can be concluded that each method of RIGC has its own merits and demerits. Nevertheless, CIGC remains the most environmentally unfriendly and the least sustainable among all methods. This is mainly due to the large detrimental waste left after reaction, causing environmental concern.

### Application of Grafted Natural Fibers in Water/Wastewater Treatment

The contamination of wastewater by a number of toxic pollutants (heavy metals, dyes, oils, etc.) is a serious environmental problem that has drawn much attention at various levels and led to imposition of more stringent regulations for discharging wastewater to eliminate their harmful effects on human and other living species [13]. Adsorption is an interesting technology that has been developed to remove such toxic pollutants from wastewater and has been used successfully for many years. Progress in this technology is dependent on the development of new adsorbents with high adsorption capacity and fast kinetics [103]. The use of NFs and agro-waste provides an alternative adsorbent materials operating by biosorption since NFs are environmentally friendly, cheap, and abundant [104]. However, biosorption is not sufficient to support scaling of treatment process and thus, NFs are often functionalized to enhance their sorption properties. In particular, there has been considerable research work focused on the use of both natural materials and their modified counterparts for wastewater treatment [105].

### Removal of Heavy Metal Ions

Heavy metals such as Cu, Zn, Cd, Pb, Ni, Co, Hg, Fe, Cr, and As are highly toxic contaminants produced by evolution of various industrial activities including tanneries, mining,

**Table 3** Summary of advantage and disadvantages of various graft copolymerization methods

Treatment	Advantages	Disadvantages	Remarks
CIGC	It uses cheap chemical initiators and is effective in achieving significant grafting levels	<ul style="list-style-type: none"> <li>- Leaves residues, which causes an environmental pollution</li> <li>- Difficult to control grafting yield</li> </ul>	Green solvents should be used
RIGC	Simple and very fast when EB is used. Allows surface as well as bulk grafting. Leaves no detrimental residues	<ul style="list-style-type: none"> <li>- High cost of infrastructure for irradiation facilities</li> <li>- Grafted materials are likely to sustain mechanical damage when high doses and dose rates are used</li> </ul>	Radiation-induced emulsion graft copolymerization provides an interesting solution to significantly reduce monomer consumption, absorbed dose and improve the process economy
MAGC	It is a green method that combines chemical and thermal treatments. MW helps reactants. Accelerated reaction can be achieved	<ul style="list-style-type: none"> <li>- Longer thermal exposure decreases the moisture content</li> <li>- It leads to changes in the physical and chemical composition of the fibers</li> </ul>	Microwave energy is not observed by non-polar materials. The level of heating depends on MW frequency and intensity
PIGC	Simple and can easily modify fibers surfaces	<ul style="list-style-type: none"> <li>- It yields low grafting level, which is confined to surfaces</li> <li>- It takes long treatment time</li> <li>- It requires a photo-initiator</li> </ul>	More suitable for surface modification that can help improve the mechanical properties and adhesion between the fiber and matrix. Thus, it more suitable for composite making
PsIGC	Simple process to modify the surface of NFs without any pollution and used to increase in the wettability of the fiber-matrix interface	<ul style="list-style-type: none"> <li>- It causes degradation and changes on the surface because of etching mechanism generating pits on the fibers surface area</li> </ul>	More suitable for bio-composites. Grafted NFs have stronger interaction with the matrix and enhanced mechanical interlocking of fiber-matrix in the composites

pesticides, batteries manufacturing, fertilizer production, and paper industries, which are posing direct risk to human and other forms of life [64]. Thus, removal of such heavy metals ions from industrial wastewater is an essential step before effluent discharge to eliminate their toxicity and meet legislation imposed by environmental agencies in many countries. Ion exchange resins are widely used materials for heavy metals removal from water and wastewater. However, commercial resins have some limitations not only in terms of slow kinetics and longer regeneration time but also pertaining the capital and operational costs of ion exchange systems.

Alternative, inexpensive adsorbents, derived from NFs, agricultural waste, and modified biopolymers have been widely investigated for the removal of heavy metals from metal-contaminated wastewater [106–108]. Fibrous adsorbents provide alternative materials with faster kinetics and ease of separation after treatment [109]. Such advantages can be boosted using NFs, which can be shredded into short rods or waved to form fabrics allowing easy flow through

formation fibrous filters. Thus, the interest of using functionalized NFs and biopolymers for heavy metal removal have been growing [110]. Metals get bound to functional group imparted to NFs using two different mechanisms: (i) chemisorption by ion exchange, complexation/coordination or chelation and (ii) physical adsorption mainly by hydrogen bonding interactions [111]. The adsorption mechanism of chemisorption depends on the ionic group fixed on grafted NFs and the valency of incoming metal ions. A schematic representation of various mechanisms for chemisorption of heavy metals ions on adsorbents is given in Fig. 7.

A wood pulp-based adsorbent was prepared by RIGC of AA under controlled conditions [112]. The poly(AA) containing adsorbent was tested for removal of some heavy metal ions such as  $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  from aqueous solutions. The maximum adsorption capacity was 7 mg/g for  $\text{Fe}^{3+}$ , 7 mg/g for  $\text{Cr}^{3+}$ , 4 mg/g for  $\text{Cd}^{2+}$  and 6 mg/g for  $\text{Pb}^{2+}$ . Similar poly(AA)-containing adsorbent prepared by RIGC of AA on jute fibers using simultaneous irradiation with  $\gamma$ -rays was tested for adsorption of  $\text{Hg}^{2+}$  and  $\text{Pb}^{2+}$  from

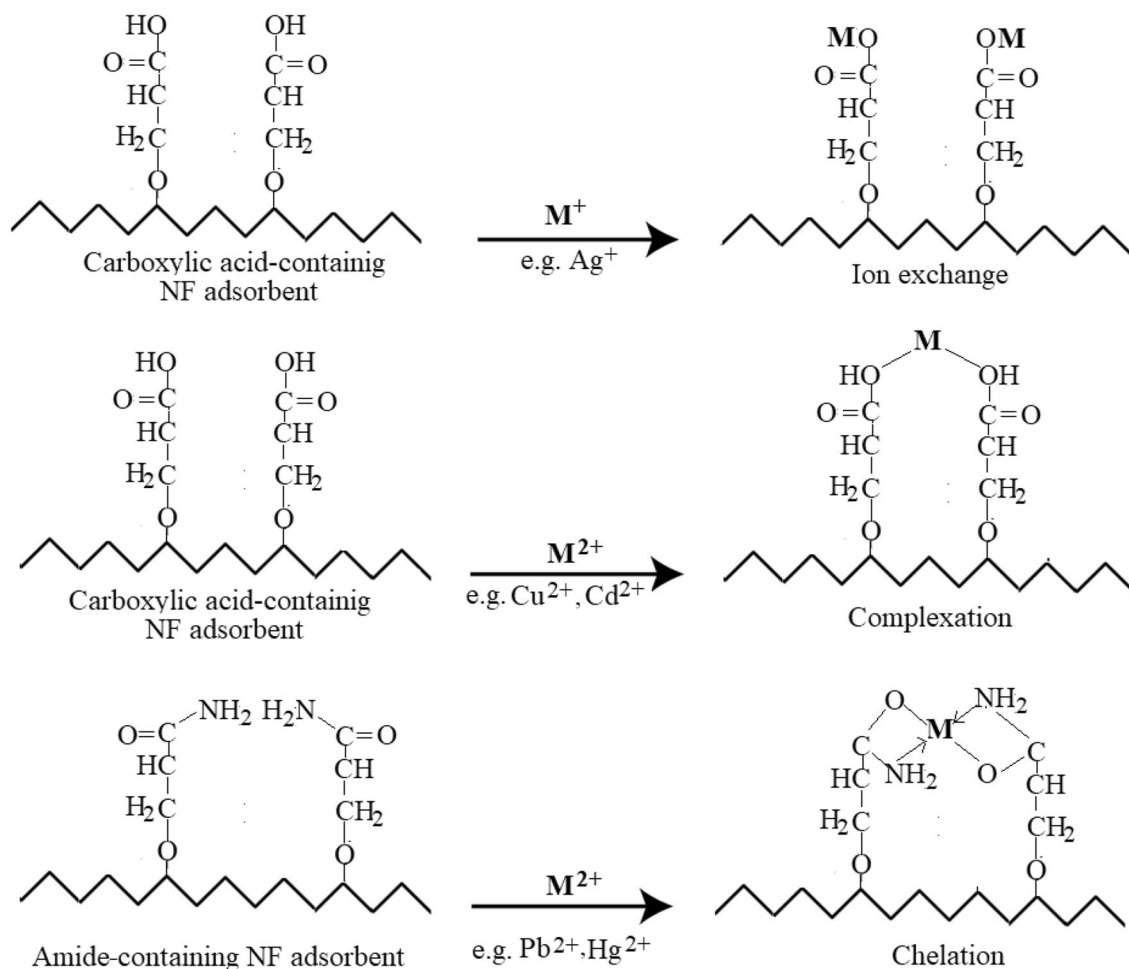


Fig. 7 Various mechanisms for adsorption of heavy metal ions by chemisorption

aqueous media [113]. The adsorption isotherms and kinetics were investigated and found to follow Langmuir isotherm and second order kinetics. The adsorbent displayed removal efficiencies of 86 and 80% for  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$  at pH 5 and 6, respectively [114].

Bao-Xiu et al. [115] prepared a cellulose-based adsorbent by MAGC of AA and AAm onto cellulose fibers and evaluated it for removal of  $\text{Cu}^{2+}$  from wastewater. The maximum adsorption capacity at the optimal adsorption conditions was 49.6 mg/g. Another adsorbent for  $\text{Cu}^{2+}$  adsorption incorporating poly(AN)-grafted cyanoethyl cellulose (CE-Cell) that was grafted through xanthate method was also investigated [116]. The hydrolyzed and grafted forms of CE-Cell showed promising  $\text{Cu}^{2+}$  adsorption results. Singha and Guleria [117] also investigated the adsorption of  $\text{Cu}^{2+}$  on a new adsorbent obtained by modification of Okra fibers by CIGC of MMA/AAM mixture using ascorbic acid/ $\text{H}_2\text{O}_2$  as a redox initiator under controlled conditions (45 °C for 90 min.). The adsorption of  $\text{Cu}^{2+}$  on the grafted adsorbent followed the Langmuir adsorption equilibrium model and demonstrated an adsorption capacity of 33.05 mg/g compared to 4.89 for the pristine Okra fiber.

Sekine et al. [103] investigated two amine-containing adsorbents for removal of  $\text{Hg}^{2+}$  from aqueous solutions. The adsorbents were prepared by RIGC of GMA onto nonwoven cotton fabric followed by treatment with ethylenediamine (EDA) or DETA. The adsorbent with EDA showed higher  $\text{Hg}^{2+}$  distribution coefficients than that of DETA-type under static conditions. The EDA-type adsorbent removed  $\text{Hg}^{2+}$  from its solution of 1.8 ppm at a space velocity of  $100 \text{ h}^{-1}$ , which corresponds to 16,000 times the volume of the packed granular adsorbent when tested on column basis [103]. A similar adsorbent based on cellulose fibers from water hyacinth grafted with GMA followed by treatment with EDA and sodium sulfite was tested for adsorption of  $\text{Cu}^{2+}$ ,  $\text{Cr}^{2+}$  and  $\text{Pb}^{2+}$  from solutions [118, 119]. The mixture of GMA with AA were grafted onto Abaca/polyester non-woven fabric followed by amination and the obtained adsorbent showed a strong affinity to  $\text{Ni}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Pb}^{2+}$  [120].

An adsorbent for removal of  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  ions from an aqueous solution was prepared by treatment of cellulose fabric with UV/ozone radiation followed by finishing with chitosan (2% w/v) in presence of hypophosphite as catalyst and citric acid as crosslinker [121]. The adsorbent optimum performance was obtained at pH of 9, adsorbent/liquor ratio of 1:20 and metal concentration of 200 g/L for 120 min at ambient temperature. The treated cotton fabrics displayed higher heavy metal adsorption compared to the untreated counterpart.

A radiation-grafted polymeric adsorbent prepared by RIGC of GMA onto cotton fabric followed by sulfonation was tested for the removal of cobalt and phenols from aqueous solutions. The adsorption of  $\text{Co}^{2+}$  was rather pH

dependent and equilibrium adsorption capacity of  $\text{Co}^{2+}$  at pH 3, 4, and 5 were 78, 83 and 91%, respectively [122].

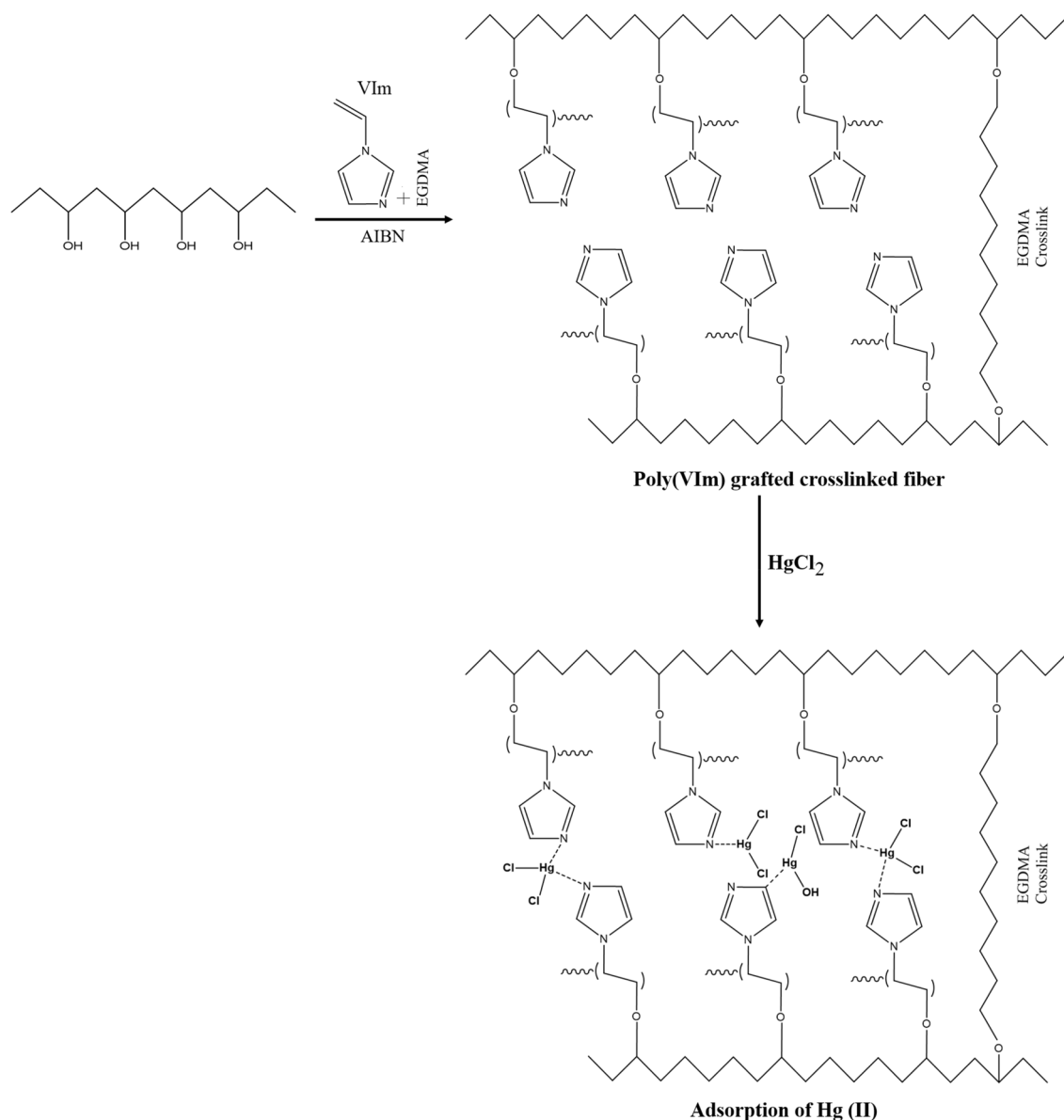
In another study, an adsorbent was made of cellulose from mercerized Ramie fibers modified with aminopoly-carboxylic acid (APCA) chelating agents such as ethylene glycol-bis (2-aminoethylether)-*N,N,N',N'*-tetra-acetic acid (EGBAEETAA). The resulting material was tested for the removal of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  ions from aqueous solutions and showed maximum adsorption capacities of 159.11 and 273.78 mg/g, respectively [123].

An adsorbent obtained by chemical modification of cellulose isolated from *Hibiscus sabdariffa* fibers via CIGC was reported [124]. The modified adsorbent exhibited higher adsorption capacity for  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  compared the unmodified counterpart. However, the adsorbent showed higher tendency to adsorb  $\text{Pb}^{2+}$  compared to  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$ . Two adsorbents based on cellulose extracted from rice straw and grafted with 2-acrylamido-2-methylpropane sulfonic acid (AASO<sub>3</sub>H) and its binary mixture with acrylonitrile (AN) showed high affinity towards  $\text{Pb}^{2+}$ . The Cellulose-*g*-AASO<sub>3</sub>H showed a maximum adsorption capacity of 154.32 mg/g which increased to 181.49 mg/g for Cellulose-*g*-AASO<sub>3</sub>H-*co*-AN [125].

In another study, functionalized wool fibers modified by CIGC that was initiated by  $\text{KMnO}_4$  and oxalic acid combined redox initiator system was used for the removal of  $\text{Hg}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Co}^{2+}$  from their aqueous solutions [126]. The modified grafted fibers showed higher adsorption affinity towards  $\text{Hg}^{2+}$  relative to  $\text{Cu}^{2+}$ , and  $\text{Co}^{2+}$ .

Another adsorbent based on wool fibers modified by CIGC of EA using redox system comprising of potassium persulfate initiator and Mohr's salt redox in an aqueous medium. The grafted wool fibers were partially converted into hydrazide and then to hydrazine by reaction with Isatin solution [127]. The adsorbent was tested for removal of  $\text{Hg}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Ni}^{2+}$  and recorded adsorption capacities of 142.5 mg/g, 49.3 mg/g, and 46.7 mg/g, respectively.

An interesting adsorbent for removal of  $\text{Hg}^{2+}$  of a recycled nature was prepared by graft copolymerization of 1-vinylimidazole (VIm) on Kapok fibers in presence of a crosslinker. The adsorbent displayed not only high  $\text{Hg}^{2+}$  selectivity but also fast adsorption kinetics and enhanced adsorption capacity of 697 mg/g. A Plausible mechanism for preparation of crosslinked and poly(VIm) grafted Kapok fibers and  $\text{Hg}^{2+}$  adsorption is shown in Fig. 8. The crosslinked and grafted adsorbent could be used for several adsorption–desorption cycles without significant loss in its capacity. This suggests that such green and economical adsorbent has potential for application in water treatment and provides an effective way to utilize NFs [128]. Similar, NF-based adsorbent containing poly(AAm-*co*-AN) grafts obtained by CIGC of AAm/AN mixture onto Psyllium husk under optimum conditions was tested for



**Fig. 8** Plausible mechanism for preparation of crosslinked and poly(VIm) grafted Kapok fibers and Hg (II) adsorption

adsorption of  $\text{Hg}^{2+}$ . The adsorbent displayed 93% removal efficiency for  $\text{Hg}^{2+}$  from solutions with the adsorption equilibrium fitted the Langmuir model coupled with second order kinetics [129].

An amidoxime-containing wool fibers prepared in 2-steps involved grafting of AN and treatment with alcoholic hydroxylamine (HA). The adsorbent showed a strong affinity to some heavy metal ions and the adsorption capacity was found to be in the order of  $\text{Hg}^{2+} > \text{Pb}^{2+} > \text{Cd}^{2+}$  [130]. Similar amidoximated adsorbent based on jute fibers grafted with AN using RIGC, followed by conversion of the nitrile groups into amidoxime groups was tested

for adsorption of some heavy metals from solutions. The amidoximated jute fibers showed a strong affinity towards some heavy metals from solutions with a variation in the adsorption capacities following the order of:  $\text{Fe}^{2+} > \text{Pb}^{2+} > \text{Cu}^{2+} > \text{Ni}^{2+}$  [131].

$\text{Cr}^{6+}$  is a higher form of chromium that is extremely toxic (1000 times greater) compared to  $\text{Cr}^{3+}$  which is found in aqueous media and its level depends on the pH of the solution. Thus,  $\text{Cr}^{6+}$  must be reduced to the permissible level (0.2 mg/L) in discharged streams to prevent its adverse effects [132]. Hajeeth et al. [133] prepared a low-cost adsorbent for  $\text{Cr}^{6+}$  removal by CIGC of AN

onto cellulose obtained from the sisal fibers. Removal efficiency of 86% was achieved after 300 min. The adsorption equilibrium followed the Freundlich isotherm and kinetically it fitted pseudo second-order model.

An attempt to remove Arsenic ( $\text{As}^{4+}$ ), which originates from mines wastewater, hot springs and natural water springs was also reported by Hoshina et al. [134]. They investigated radiation grafted cellulosic adsorbent prepared by RIGC of 2-hydroxyethyl methacrylate phosphoric acid (HEMA) monomer onto nonwoven cotton fabric and subsequent loading of 0.38 mmol/g Zr on the grafted chains [134]. Interestingly, an adsorption capacity of the 0.1 mmol/g was reached at a feed solution containing 1 mg/L of  $\text{As}^{4+}$  at  $1000 \text{ h}^{-1}$  space velocity and

pH value of 2. Such adsorption performance is 100 times faster than commercially available resins. A summary of previous studies on functional grafted adsorbents based on NFs for heavy metals removal is presented in Table 4. It can be concluded that majority of the investigated adsorbents are based on plant NFs and several agriculture by-products compared to fewer investigation on adsorbents based modified wool fibers. Furthermore, NFs modified with various graft copolymerization methods are interesting adsorbents for heavy metal ions removal from aqueous media not only because of higher adsorption capacity compared to the bio-sorption of their pristine counterparts but also due to their potential for the development of inexpensive adsorbents.

**Table 4** Summary of previous studies on functional grafted adsorbents based on NFs for heavy metal removal

Fiber type	Grafting method	Initiator	Monomer	Type of heavy metals	References
Abaca	RIGC	EB	GMA	$\text{Cu}^{2+}$ and $\text{Ni}^{2+}$	[135]
Abaca/polyester non-woven	RIGC	EB	GMA	$\text{Ni}^{2+}$ , $\text{Cd}^{2+}$ , and $\text{Pb}^{2+}$	[120]
Cellulose	MAGC	Potassium persulfate	AA and AAm	$\text{Cu}^{2+}$	[115]
Cellulose	CIGC	Potassium persulphate	AASO <sub>3</sub> H and AN	$\text{Pb}^{2+}$	[125]
Chitosan	CIGC	Ceric ammonium nitrate	MAN	$\text{Pb}^{2+}$	[136]
Cyanoethyl cellulose	Xanthate method	Hydrogen peroxide	AN	$\text{Cu}^{2+}$	[116]
Wood pulp	RIGC	EB	AA	$\text{Fe}^{3+}$ , $\text{Cr}^{3+}$ , $\text{Pb}^{2+}$ , $\text{Cd}^{2+}$	[112]
Cotton fibers	CIGC	Sodium periodate	MA/DETA	$\text{Cu}^{2+}$ and $\text{Pb}^{2+}$	[137]
Cotton fabric	RIGC	EB	GMA	$\text{Hg}^{2+}$	[103]
Cotton fabric	RIGC	$\gamma$ -rays	GMA	$\text{Co}^{2+}$	[122]
Cotton fabric	RIGC	EB	HEMA/phosphoric acid/Zr	$\text{As}^{4+}$	[134]
<i>Hibiscus sabdariffa</i> cellulose	PIGC	Chloroacetyl chloride	EDA	$\text{Pb}^{2+}$ , $\text{Cu}^{2+}$ and $\text{Cd}^{2+}$	[124]
Hydroxypropyl cellulose	CIGC	Ammonium persulphate	AAm	$\text{Pb}^{2+}$ , $\text{Cu}^{2+}$ and $\text{Cr}^{3+}$	[138]
Jute fibers	RIGC	$\gamma$ -rays	n-BMA	$\text{Cu}^{2+}$	[139]
Akra fibers	CIGC	Ascorbic acid/ $\text{H}_2\text{O}_2$	MMA/AAm	$\text{Cu}^{2+}$	[117]
Jute fibers	RIGC	$\gamma$ -rays	AA	$\text{Hg}^{2+}$ and $\text{Pb}^{2+}$	[113]
Jute fibers	RIGC	$\gamma$ -rays	AN	$\text{Fe}^{2+}$ , $\text{Pb}^{2+}$ , $\text{Cu}^{2+}$ and $\text{Ni}^{2+}$	[131]
Kenaf cellulose	CGC	Ceric ammonium nitrate	AN	$\text{Cu}^{2+}$ , $\text{Fe}^{3+}$ , $\text{Co}^{3+}$ , $\text{Mn}^{2+}$ , $\text{Cr}^{3+}$ , $\text{Ni}^{2+}$ and $\text{Zn}^{2+}$	[140]
<i>Luffa cylindrica</i> fibers	CIGC	Chromic acid	AA	$\text{Mg}^{2+}$ , $\text{Ni}^{2+}$ and $\text{Zn}^{2+}$	[141]
Ramie fibers	CIGC	Anhydrous pyridine	EGTAD	$\text{Cd}^{2+}$ and $\text{Pb}^{2+}$	[123]
Water hyacinth	RIGC	$\gamma$ -rays	GMA	$\text{Pb}^{2+}$ , $\text{Cu}^{2+}$ and $\text{Cr}^{3+}$	[119]
Wood pulp	RIGC	EB	AA	$\text{Fe}^{3+}$ , $\text{Cr}^{3+}$ , $\text{Pb}^{2+}$ , $\text{Cd}^{2+}$	[112]
Cellulose from sisal fibers	CIGC	Ceric ammonium nitrate	AN	$\text{Cr}^{6+}$	[133]
Wool fibers	CIGC	$\text{KMnO}_4$ and oxalic acid	AN	$\text{Hg}^{2+}$ , $\text{Cu}^{2+}$ , and $\text{Co}^{2+}$	[126]
Wool fibers	CIGC	Potassium persulphate	EA	$\text{Hg}^{2+}$ , $\text{Cu}^{2+}$ , and $\text{Ni}^{2+}$	[127]
Kapok fibers	CIGC	2,2'-azobis(2-methylpropionitrile)	VIm	$\text{Hg}^{2+}$	[128]
Psyllium	CIGC	Ceric ammonium nitrate	AAm/AN	$\text{Hg}^{2+}$	[129]
Wool fibers	RAFT	$\alpha$ , $\alpha'$ -Azodiisobutyramidine dihydrochloride	AN	$\text{Hg}^{2+}$ , $\text{Pb}^{2+}$ , $\text{Cd}^{2+}$	[130]

## Removal of Dyes

The use of synthetic dyes is widespread in various industries including textiles, plastics, and papers productions. Disposal of such toxic pollutants to water bodies is harmful not only to aquatic life but also to human, animals, and the whole ecosystem. Thus, removal of dyes from the industrial wastewater has been a challenging task among researchers that is receiving utmost interest in the field of water treatment. More details on various aspects of pollution by various streams, adverse effects on human health and the environment and the various methods of treatments can be found elsewhere [142]. The use of cellulose-based adsorbents for the removal of dyes from water has been vastly investigated to seek effective and cheap solution for such a problem [143].

Functional monomers such as AA and MAA that can directly confer carboxylic acid group to polymer substrates in a single step have been frequently used to prepare adsorbents for dye removal from aqueous media [44]. Dafader et al. [144] prepared fibrous adsorbent by RIGC of AA onto cotton threads and tested it for removal of methylene blue from aqueous media. The adsorbent recorded a dye adsorption capacity reaching a value of 16.86 mg/g and the dye removal efficiency was a function of its concentration in the solution. On the other hand, the affinity of poly(AA) modified wool fibers obtained by RIGC of AA onto wool fibers towards basic dyes was greatly enhanced by the incorporation of this ionic group [72]. Earlier, an adsorbent obtained by RIGC of another carboxylic acid containing monomer (IA) onto cellulosic fabric waste was tested for removal of methylene blue [145] from aqueous solution with a maximum adsorption capacity of 38 mg/g [146].

Another cellulose-based adsorbent obtained by CIGC of AA onto cellulose from the empty fruit bunch using potassium bromate/thiourea dioxide as an initiator was prepared and tested for adsorption of methylene blue dye by Abdel-Halim et al. [147]. A complete and fast removal of methylene blue dye and Pb could be achieved in 35–45 min reflecting a strong potential of the investigated adsorbent for wastewater treatment. In a similar manner, Zhang et al. [148] earlier prepared a carboxylic acid-containing adsorbent by CIGC of AA onto chloromethyl cellulose (CM-Cell) using APS as an initiator and studied its performance for adsorption of few dyes. The prepared adsorbent showed a strong affinity towards methyl orange, disperse Blue 2BLN and malachite green chloride reaching removal efficiencies of 84.2%, 79.6% and 99.9%, respectively.

Gupta et al. [141] used cellulosic *Luffa cylindrica* as a substrate for preparation an adsorbent containing poly(AA) for the removal of methylene blue and some heavy metal

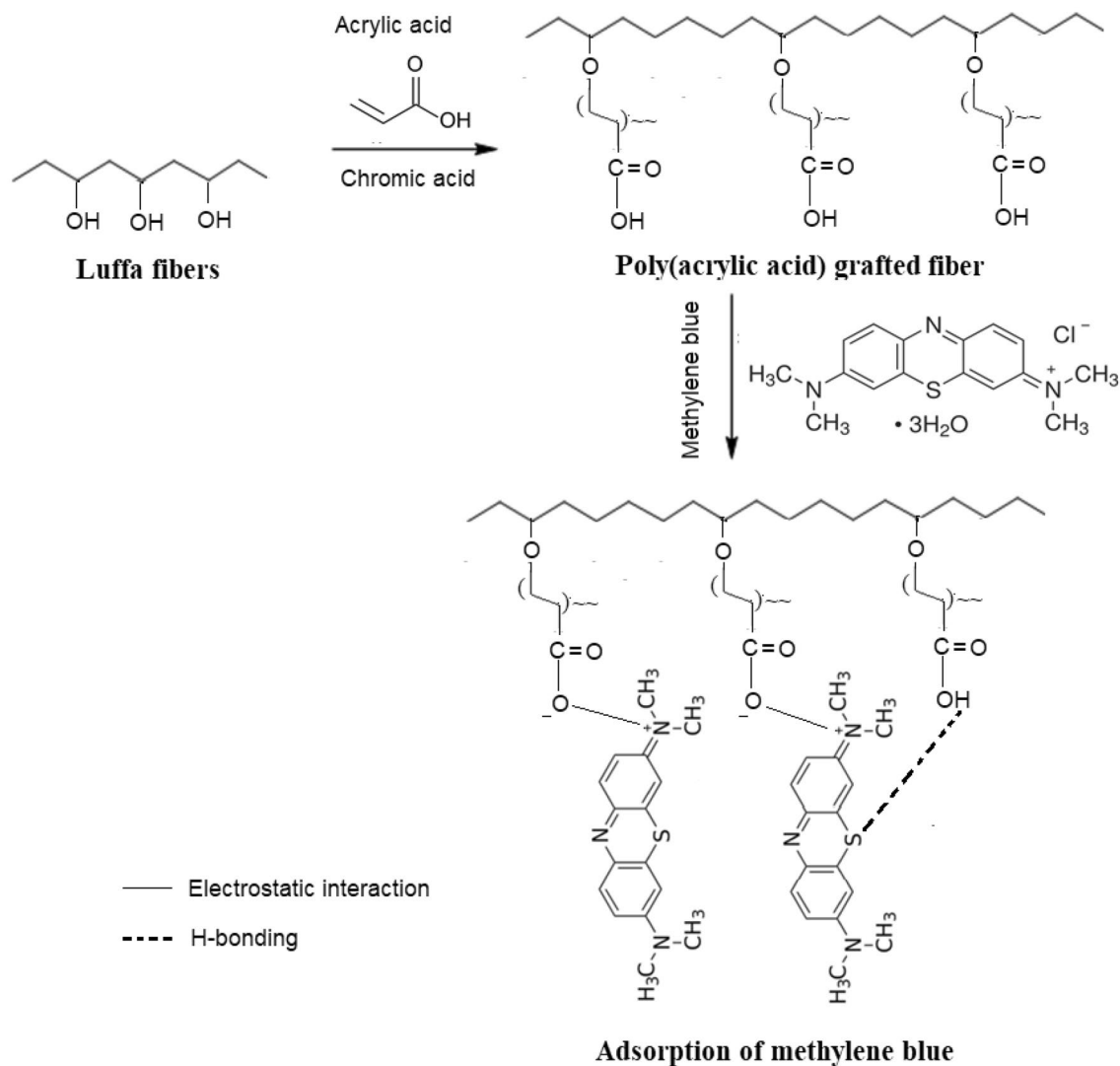
ions from wastewater. The fibrous adsorbent was obtained by grafting of AA on luffa fibers under controlled condition using chromic acid as an initiator according to the suggested mechanism presented in Fig. 9. The maximum adsorption capacity of the dye was mounted to 62.15 mg/g at an equilibrium time of 175 min. A maximum removal efficiency of 45.8% was observed for  $Mg^{2+}$  compared to other metal ions. These authors extended their application for *Luffa Cylindrica* fibers as substrate for preparing a new adsorbent by grafting of MA/AAm using MAGC without any initiator. The adsorption capacity of the adsorbent was for removal of Congo red dye from aqueous solution. The maximum adsorption capacity of the dye was 17.39 mg/g [149].

Delignified *Grewia optiva* fibers were also used to prepare another grafted adsorbents by MAGC of comonomer combinations such as MMA with either EM or EA using ascorbic acid/ $H_2O_2$  as the initiator [82]. The yielded adsorbent showed an enhanced methylene blue from aqueous system compared to the pristine fibers. Methylene blue was also removed from aqueous solution by another adsorbent of modified *Hibiscus cannabinus* as reported by Sharma et al. [150]. To function as an adsorbent, the *Hibiscus cannabinus* fibers were modified by CIGC of AA and AA/AAm mixture using ceric ammonium nitrate/nitric acid initiator. The poly(AA) grafted fibers showed slightly better methylene blue adsorption than those grafted with AA/AAm but both grafted fibers performed better than the pristine *Hibiscus cannabinus* fibers.

The potential of cellulose-based adsorbent prepared by graft copolymerization of GMA and treatment with diethylenetriamine pentaacetic acid (DETAPAA) was tested for removal of cationic dyes such as malachite green and basic fuchsine was investigated by Zhou et al. [55]. The obtained adsorbent outperformed the corresponding adsorbents reported in the literature and displayed an adsorption capacity as high as 1155.76 mg/g for basic fuchsine compared to 458.72 mg/g for malachite green at a concentration of 2000 mg/L in the treated solution.

Goel et al. [151] developed an adsorbent based on the waste of cotton fabric by RIGC of 2-(methacryloyloxy) ethyltrimethylammonium chloride (MAOETMAC) in a single step reaction. The adsorbent was tested for adsorption of acid blue 25 and acid blue 74 dyes. The adsorbent having 25% grafting level showed higher removal capacity for acid blue 25 (~ 540.0 mg/g) than acid blue 74 (~ 340.0 mg/g). Earlier, these authors [152] also grafted vinylbenzyltrimethyl ammonium chloride (VBTMAC) onto cotton fabric using RIGC and tested the obtained adsorbent for the removal of several cationic dyes. The adsorbent exhibited equilibrium adsorption capacities close to 540, 474 and 122 mg/g for acid blue 25, acid yellow 99 and acid blue 74, respectively.





**Fig. 9** Plausible mechanism for grafting of AA on luffa fibers and adsorption of methylene blue by poly(AA) containing adsorbent

In a recent study, a new adsorbent based on cellulose extracted from rice straw that was grafted with  $\text{AASO}_3\text{H}$  and its binary mixture with AN showed a strong affinity towards cation dyes such as malachite green and crystal violet. The adsorbents showed higher affinity to malachite green compared to crystal violet following the order cellulose < cellulose-*g*- $\text{AASO}_3\text{H}$ /AN.

Cellulose-*g*- $\text{AASO}_3\text{H}$  [125]. A summary of previous studies on functionalized grafted adsorbents based on NFs for dye removal is presented in Table 5. It can be observed that NFs and cellulose extracted from agricultural waste were modified with various monomers imparting either anionic or cationic characters to encounter basic or acid dyes. No animal or silk fibers were reported to be modified for dye removal application despite the presence of

many reports on dyeing of wool and silk with reactive dyes [153–155]. In conclusion, the modified NFs have a strong potential for dye removal from aqueous media cheap chelating materials.

### Removal of Oil Spill

The oil spill generated by industrial activities is causing a severe pollution to various water bodies and posing adverse impacts on human and marine life. Oil spill treatment by adsorption is an interesting method that is receiving increasing attention. A majority of the oil spill adsorbents are synthetic materials and thus their disposal possibilities are limited [158]. Plant fibers and cellulose

**Table 5** Summary of previous studies on functional grafted adsorbents based on NFs for dye removal

Natural fibers	Grafting method	Initiators	Monomers	Dye types	References
Carboxymethyl cellulose	CIGC	Ammonium persulfate	AA	Methyl orange, disperse Blue 2BLN and malachite green chloride	[156]
Cellulose (palm tree waste)	CIGC	Potassium bromate	AA	Methylene blue	[147]
Cellulosic fabric	RIGC	$\gamma$ -rays	IA	Methylene blue	[146]
Cellulose	CIGC	Sodium hydroxide	GMA and DETAPAA	Malachite green and basic fuchsine	[55]
Cellulose	CIGC	Potassium persulphate	AASO <sub>3</sub> H/AN	Malachite green and crystal violet	[125]
Cellulosic cotton fabric	RIGC	EB	MAOETMAC	Acid Blue 25 (AB25) and Acid Blue 74 (AB74)	[151]
Cotton	RIGC	$\gamma$ -rays	AA	Dye from aqueous medium	[144]
Cotton cellulose	RIGC	$\gamma$ -rays	VBTMAC	Acid dyes, AB25, AY99 and AB74	[152]
<i>Grewia optiva</i> fibers	MAGC	Ascorbic acid/H <sub>2</sub> O <sub>2</sub>	MMA, EMA or EA	Methylene blue	[82]
<i>Hibiscus canabius</i> fibers	CIGC	Ceric ammonium nitrate/HNO <sub>3</sub>	AA or AA/AAm	Methylene blue	[150]
Jute fibers	RIGC	$\gamma$ -rays	AA	Reactive dye from wastewater	[157]
<i>Luffa cylindrica</i> fibers	CIGC	Chromic acid	AA	Methylene blue	[141]
<i>Luffa cylindrica</i> fibers	MAGC	No initiator	MA/AAm	Congo red dye	[149]
Wool fibers	RIGC	$\gamma$ -rays	AA	Safranin-O dye and oil Red EGN dye	[72]

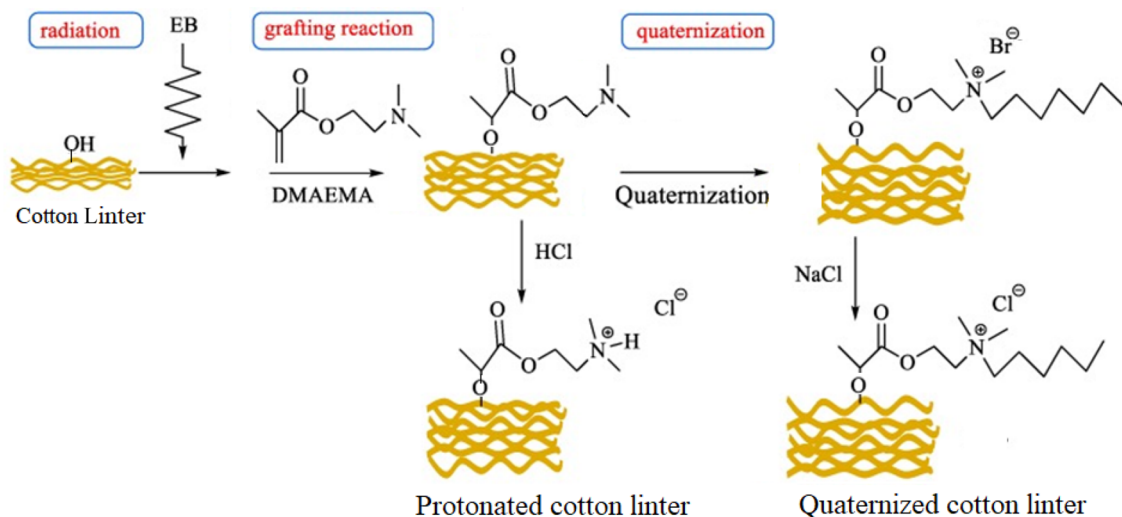
based sorbents are alternative environmentally friendly and cheap materials that have a strong potential for the application in oil spill clean-up [145, 159, 160]. However, they must undergo prior chemical treatments to enhance their oleophilicity, which is limited by their tendency to have competitive sorption between water and oil. Chemical modifications of NFs such as cotton include acylation of cellulose with fatty acid [161] or treatment with acetic anhydride [162]. Moreover, thermal treatment of cotton fibers with polyester can also enhance their sorption to diesel oil. This adsorbent showed 99% efficiency that represented 20 times weight increase of the sorbent original weight [163].

Graft copolymerization with hydrophobic monomers such as styrene and BA was also used to modify NFs to boost their hydrophobicity and oleophilicity. Wang et al. [164] studied an oil sorbent prepared by RIGC of styrene on Kapok fibers. The incorporated polystyrene endowed higher toluene sorption rate and capacity compared to the pristine fibers. Particularly, the adsorbent exhibited a remarkable toluene sorption capacity of 43.2 g/g and reached an absorption equilibrium within 15 min. BA was also grafted on cotton fibers using MACG method as reported by Gao et al. [165]. The sorbent showed 3–4 times higher oil sorption capacity compared to the pristine cotton fibers, which is mounted to 13.83 g/g for benzene and 11.23 g/g for an edible oil.

Other fibers such as banana fibers were also used to develop an adsorbent of oil removal by grafting of BA [166]. The new adsorbent showed higher adsorption capacity than the original banana fibers, which reached a maximum value of 14.15 g/g coupled with a reasonable reusability. Another oil sorbent based on nettle fibers modified by grafting BA was investigated by Viju et al. [167]. The fibrous adsorbent showed higher sorption capacity towards crude oil and vegetable oil compared to both the pristine and commercial polypropylene counterparts with a remarkable stability. The potential of grafted nettle fibers was evident from the sorption capacity that reached of 36.60 g/g and 25.56 g/g for crude oil and vegetable oil, respectively. It can be concluded that graft copolymerization with hydrophobic monomers is an effective method for imparting hydrophobicity and oleophilicity to cellulosic fibers and promoting their application as cheap oil spill clean-up materials.

## Removal of Other Toxic Pollutants

Toxic pollutants such as cyanides and dichromate anions were removed from aqueous solution by chelating cellulosic adsorbents prepared by RIGC of AN and AASO<sub>3</sub>H onto cotton fabric followed by treatment with HA to introduce



**Fig. 10** Procedure for the preparation of cotton linter-based adsorbents [171]

amidoxime group [168]. The removal of cyanide reached 89% efficacy compared to that of dichromate which stood at 65%.

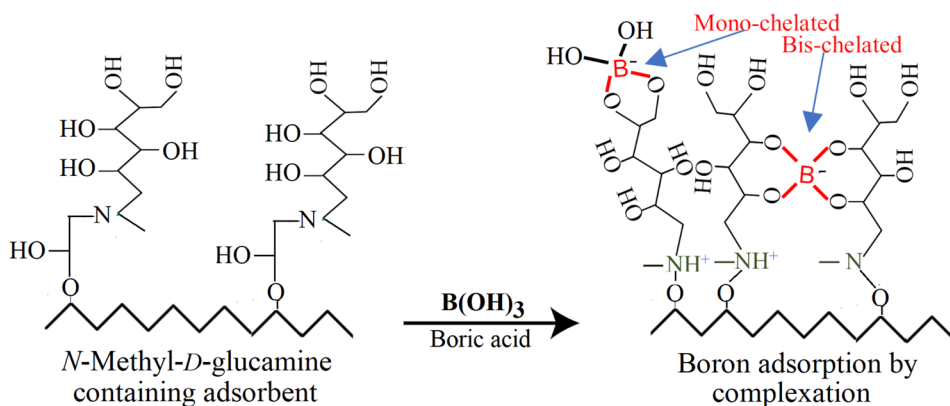
Removal of phenol and pesticide molecules such as 2,4-dichlorophenoxyacetic acid (DCPAA) was investigated by adsorbent prepared by RIGC of GMA onto cellulose as reported by Takács et al. [169]. The adsorption of phenol was faster with the adsorption saturation achieved after 5–6 h. Despite the relatively low adsorption capacity of 4–8 mg/g, it was higher than values reported for the untreated biosorbent [169]. The adsorption of pesticide was further improved by the addition of  $\beta$ -CD [170].

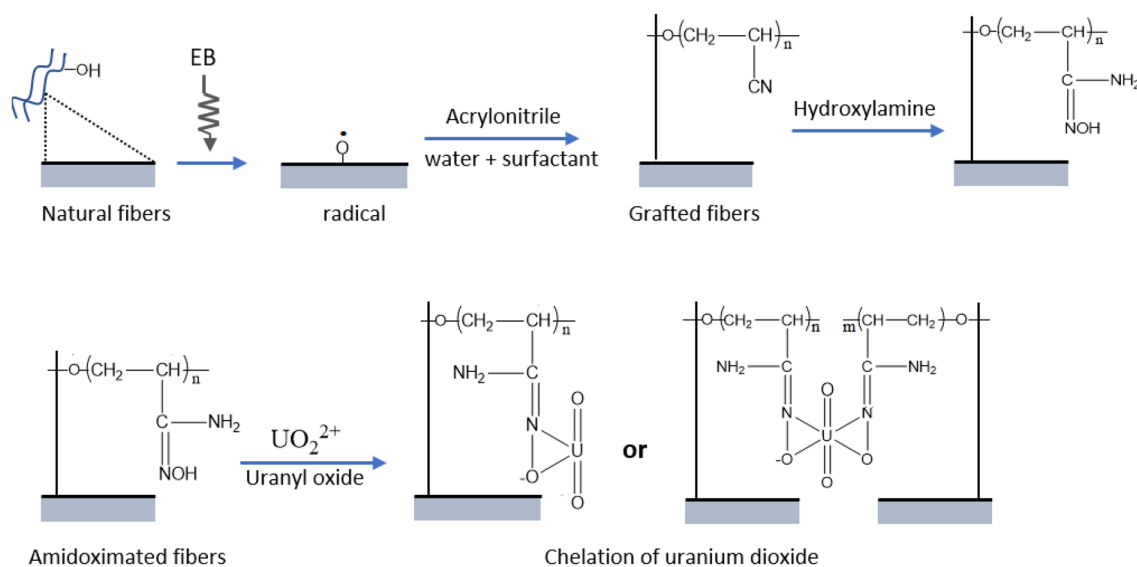
Du et al. [171] reported the preparation of cotton linter-based adsorbent for the removal of humic acids from wastewater. The adsorbent was prepared by RIGC of dimethylaminoethyl methacrylate (DMAEMA) followed by either quaternization by bromohexane or protonation with HCl as shown in the procedure presented in Fig. 10. Both adsorbents

exhibited adsorption capacities reaching 250 mg/g and 333 mg/g (at pH 6) for quaternized and protonated cotton linters, respectively.

Boron is another harmful pollutant that must be strictly reduced to few milligrams per liter in various industrially produced waters and geothermal streams and its removal can be achieved efficiently by chelating resins bearing *N*-methyl-*D*-glucamine (NMDG) [172]. Nishihama et al. [173] investigated the potential of commercial fibrous adsorbent (Chelest Fiber® GRY-HW) prepared by graft copolymerization of GMA onto cotton fabric followed by NMDG immobilization for boron removal from Salt Lake brine. The presence of polyols and tertiary amine ends in NMDG structure allowed binding boron by chelation as shown in Fig. 11. This fibrous adsorbent exhibited higher boron adsorption capacity and faster kinetics compared to commercial counterparts in the particulate form. Overall, it can be suggested that modification of NFs by graft copolymerization can host desired

**Fig. 11** Chelation of boron by NMDG containing adsorbent by complexation [173]





**Fig. 12** Mechanisms of preparation of uranium adsorbent by radiation-induced graft copolymerization of acrylonitrile and subsequent amidoximation and chelation of uranyl oxide

functionalities allowing their applications in the removal of variety of pollutants of concern from water and wastewater.

## Recovery of Precious/Rare Earth Metals

Recovery of uranium from sea water is an interesting method to meet the shortage of its mined ore and increasing demand [174]. Yin et al. [175] developed an adsorbent containing amidoxime ligands for recovery of uranium from aqueous solutions based on wool fibers modified by RIGC of AN followed by treatment with HA. The obtained adsorbent showed a strong affinity towards uranyl oxide cation present in aqueous solutions. An illustration of the mechanism of preparation of amidoxime-containing adsorbent and its uranyl oxide chelation is presented in Fig. 12. The presence of both acidic and basic parts in the amidoxime together with two lone pairs of electrons: one pair on the oxygen atom and one on nitrogen atom provided ligand for chelation of  $UO_2$ . To enhance uranium adsorption capacity, Zhang et al. [176] subjected the wool fibers to chemical treatment with urea, sodium hydroxide and sodium sulfite prior to grafting with AN followed by treatment with HA. To eliminate biofouling effect on the  $UO_2$  adsorption, grafting was combined with titania particles loading to impart antimicrobial character as reported by Wen et al. [177].

Wang et al. [178] recently prepared another amidoximated adsorbent based on cellulose fibers grafted with poly(AN) that was subsequently converted to amidoxime ligand with high affinity to  $U^{6+}$  ion. The adsorption capacity of  $U^{6+}$  ion was found to be 52.88 mg/g at pH 5 and under static conditions which was dropped to 1.22 mg/g at pH 8 when tested in a

dynamic bed column using simulated seawater. Nevertheless, these authors suggested that the adsorbent has a strong potential for scale up application for uranium recovery from seawater. The co-grafting of MAA with AN (20/80%) onto bleached and mercerized woven cotton fabric was found to enhance the adsorption of  $U^{6+}$  ions by incorporation of  $-COOH$  to amidoxime obtained after treatment with HA/alcohol according to Othman et al. [179]. The mechanism of adsorption followed a mononuclear complexation.

Monier et al. [180] studied a fibrous adsorbent based on cotton fibers that was prepared by graft copolymerization of poly(PAN) followed by loading of phenyl thiosemicarbazide (PTSC). The modified fibers were tested for the recovery of precious metal ions such as  $Au^{3+}$ ,  $Pd^{2+}$  and  $Ag^+$  from their aqueous solutions and exhibited adsorption capacities of 198.31, 87.43 and 71.14 mg/g, respectively.

An adsorbent having amidoxime ligand was also prepared by graft copolymerization of AN onto delignified kenaf fibers and subsequent treatment with HA as reported by Rahman et al. [181]. The amidoximated ligand showed high adsorption capacities for some rare earth metals such as  $La^{3+}$ ,  $Ce^{3+}$ ,  $Pr^{3+}$ ,  $Gd^{3+}$  and  $Nd^{3+}$ , which recorded values of 262, 255, 244, 241 and 233 mg/g (at pH 7), respectively.

## Challenges and Future Directions for Adsorbents Sustainability

The use of NFs substrates for the development bio-based adsorbents after modification by graft copolymerization to impart desired functional groups is an interesting approach

for wastewater treatment and environmental remediation. Various graft copolymerization methods have been successfully used for introducing ionic groups and chelating ligands to NFs, and the levels of modifications depend on the reaction conditions. However, there are several challenges that must be addressed to maintain the green chemistry concept and sustainability in the obtained adsorbents. Pertaining to modification of NFs by graft copolymerization, it can be realized that there is an environmental concern over the use of CIGC method despite its widespread applications. This is due to the large determinant waste to be left after reactions contributing to environmental pollution. Thus, it is highly recommended to replace conventional initiators and solvents with green ones and optimize reaction parameters to control grafting levels, while reducing the environmental impact associated with the waste.

The use of RIGC offers a facile method to modify NFs with a close control over grafting levels. However, the use of high energy radiation such as EB in RIGC with high doses during irradiation of NFs is likely to cause partial mechanical damage. Hence, lower doses and dose rates are preferred upon irradiation of NFs. Moreover, conducting the reactions in emulsion media is an effective way to reduce the monomer consumption and the needed irradiation dose to maintain the mechanical integrity in the obtained adsorbents and keep their cost low. On the other hand, the exposure of NFs to thermal treatment in MACG, decreases the moisture content and changes the physical structure and chemical composition of the fibers. Moreover, microwave energy is not absorbed by non-polar materials. Thus, the level of heating should be controlled, and this depends on MW frequency and intensity both require the presence of special microwave working facilities. PICG of NFs is also a simple method to modify NFs. Nevertheless, it requires the use of photo-initiators. In addition, the reaction takes a long time to achieve low grafting levels and the imparted ionic characters are only confined to top surface layers. Therefore, this technique is more suitable for surface modifications required to improve the adhesion between NFs and matrix during the fabrication of green composites. A similar recommendation can be made upon using PsICG, in which degradation and changes on the fibers' surfaces occur from the etching mechanism. Moreover, pits are generated on the fibers' surface depending on the properties of the applied plasma, thus leaving this technique more suitable for bio-composites development.

Although there is a growing concern on the use of chemical treatment for modification of NFs by graft copolymerization to enhance their adsorption capacity towards various pollutants such as dyes, heavy metal ions, oils, the replacement of petrol-based ion exchange resins with cheap and environmentally benign modified NFs not only introduces an element of green chemistry and sustainability to such materials but also promotes their application in environmental

remediation in way leading to double benefits when the agro-waste is utilized. In addition to the above-mentioned concerns related to the environmental impacts of grafting, it is notable that, up to this point, the use of adsorbent materials has not become well integrated into the commonly used wastewater treatment technologies. Instead, wastewater treatment operations have been dominated by unit operations such as gravity settling, aeration, activated sludge treatment, and anaerobic digestion [182, 183]. Though the reasons for the relatively minor usage of NFs-based adsorbents for industrial wastewater treatment may be hard to explain in detail with some contributing factors may be related to environmental issues. Particularly, there has been relatively little research attention paid to the final disposal of spent adsorbent materials after their use in collecting pollutants from water [184–186]. For example, landfilling of contaminated cellulose-based sorbent materials poses several disadvantages, including a generally high content of water, a propensity to generate methane due to anaerobic conditions of landfills, and concerns about leaching of the adsorbed pollutants. Such problems can be addressed to some extent with state-of-the-art landfill designs [187]. However, such mitigation features are likely to involve high costs. Incineration, as a possible alternative to landfilling, seems to be a poor choice for cellulose-based spent adsorbent materials due to its likely high-water content. Composting may be a suitable option for treatment of dye-contaminated cellulose-based adsorbents, but it is hard to argue that such processing would be more practical than the aerobic or anaerobic wastewater treatment operations that are in common use [183].

It is noteworthy mentioning that many of the investigated adsorbents developed based on grafted NFs were dedicated to the removal of heavy metal ions and dyes. However, most of the studies were conducted in synthetic aqueous media under static conditions without considering the dynamic behavior of the adsorbent and the presence of multiple pollutants. More work is highly needed to take such green adsorbents beyond the fundamental studies of equilibrium, kinetics, and thermodynamics of adsorption to column flow dynamics, breakthrough curves establishment and stability verification. This is highly important for practical applications.

The bio-based grafted adsorbents showed a strong potential for oil spill removal. However, the investigation of such adsorbents remains limited, and majority of them were obtained by chemical modifications of NFs. On the other hand, there is a widespread yet relatively low usage volume of cellulosic materials such as straws combined in bundles as adsorbents deployed near to storm drains (at construction sites) and as booms for the containment of oil spills at the surface of the water [188]. Such applications benefit from the incredibly low cost and environmentally benign nature of unmodified NFs. Thus, the use of very low-cost

cellulosic waste materials as sorbents to address various pollution-related problems can be regarded as a disruptive innovation, against which all higher-cost solutions, including graft-modified sorbents, will need to be compared. This requires more research efforts to explore the potential of grafted NFs for oil spill clean-up.

Recovery of precious and rare earth metals for water/wastewater is another area where grafted NFs-based adsorbents are not well explored. The use of such adsorbents provides a simple and sustainable technique for recovery of Au, Ag, Pd and U from solution. The use of techniques such as RIGC provides a convenient method to improve the selectivity and sorption capacity of NFs by imparting appropriate ligands. More work is needed to investigate factors affecting the performance of the adsorbents and how particular ligands work under dynamic conditions.

One of the new promising applications for grafted NFs is the CO<sub>2</sub> capture, which is based on chemisorption by

amine-containing materials. Biomaterial-based solid CO<sub>2</sub> adsorbents have received a little attention despite being environmentally benign. Despite the potential use of nanofibrillated cellulose in an aqueous form for preparation of CO<sub>2</sub> absorbent by freeze-drying with *N*-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane and wet impregnation of kenaf NFs with monoethanolamine or tetraethylenepentamine [189, 190], the obtained adsorbent are subjected to amine leaching leading to poor regeneration and low stability. Thus, graft copolymerization using one of the green techniques discussed in this article can provide means to achieve covalent immobilization of amine groups for CO<sub>2</sub> capture, preventing functional group leaching and enhancing the adsorbent stability. A summary of current challenges to NFs grafted adsorbents and their future research directions towards retaining sustainability are presented in Table 6.

**Table 6** Summary of current challenges and future research directions

Areas	Methods	Challenges	Future directions
Preparation of NFs-based adsorbents	CIGC	- Large determinant waste - Environmental pollution	- Use green initiator - Use green solvent
	RIGC	- $\gamma$ -rays in a radioactive source that is continuously depleting - Long time to achieve desired GY when dose rate is low - Conventional solvents are used to dilute monomers - Adsorbent preparation may need a post-grafting functionalization reaction	- Use EB accelerator - Use EB with low acceleration energy - Conduct grafting reaction in emulsion - Use functional monomer in a single-step grafting
	PIGC	- Long reaction time - Low GY	- More suitable for green composites
	PsIGC	- Long reaction time - Low GY	- More suitable for green composites
	MAGC	- Undermined by over-heating	- Use customized facilities with proper heat control
Applications of adsorbents	Adsorption mode	- Mostly carried out under static conditions only	- More work for dynamic column analysis and breakthrough curve determination
	Adsorbent stability	- Low stability	- keep modification cost low to compensate for low number of cycles
	Oil spill removal	- Few studies with adsorbent obtained by chemically initiated grafting	- Use NFs in bundles without modification - Use single step radiation-initiated grafting with EB
	Recovery of precious metals	- No sufficient studies	- More studies with adsorbents prepared single step radiation-initiated grafting with EB
Disposal of spent adsorbents	CO <sub>2</sub> capture	- No sufficient studies	
	- Normal landfill - Incineration	- Leaching of sorbed pollutants - High content of water	- Use robust landfill - Replace incineration with composting

## Conclusions

Graft copolymerization initiated by various techniques including chemical, photochemical, radiochemical, thermal, and plasma initiations is an appealing method for imparting desired ionic moieties to NFs without compromising their inherent properties. CIGC is a well-established method that confers NFs favorable pollutant affinity properties, but it is challenged by the environmental pollution with the post-reaction residues. Alternatively, RIGC is appealing for incurring grafts from surface to core of NFs allowing greater control on GY to suit adsorbents and is more sustainable when carried out in emulsion media. MAGC, PIGC and PSIGC were found to be green ecofriendly methods promoting less monomer consumption and minimum residue production. While MAGC can impart considerable modification favoring adsorption, PIGC and PSIGC are less likely to be suitable for converting NFs to effective adsorbents due to low GY. The incorporation of functionalized grafts into NFs endowed new active binding sites that greatly enhance their pollutant-binding capacity leading to superior selective adsorbents with tunable end-uses compared to their pristine counterparts. The modified NFs found applications in water/wastewater decontamination including removal of heavy metal ions, dyes, oil spills, and other pollutants in addition to extraction of precious metals from aqueous media. The use of NFs provides double environmental mitigation approaches that are utilizing agricultural waste and treating a variety of pollutants in wastewater. Despite the presence of some critical challenges, further advances in the preparation and applications of grafted NFs for water and wastewater would be realized. This can be accelerated not only by maintaining the green chemistry of the developed grafted NFs adsorbents and keeping their cost low but also by enhancing their stability and exploring new horizon for their potential applications as well as scaling their performance under dynamic conditions.

**Acknowledgements** The authors wish to acknowledge the financial support by Malaysia-Thailand Joint Authority (MTJA) research Grant (Vote. No. R.J130000.7609.4C172). N.A. Zubair is grateful for Malaysia-Japan International Institute of Technology (MIIT) for the Student Incentive Excellence Scheme.

**Author Contributions** Idea conceived by MMN. RMM, NAZ, MZ, MMN and MH wrote the article. MMN and MH revised and edited the article.

**Funding** This project is supported by Malaysia-Thailand Joint Authority (MTJA) research Grant of vote. No. R.J130000.7609.4C172.

## Declarations

**Conflict of interest** The authors declare that they have no conflict of interest.

## References

1. Thomas B, Raj MC, Athira KB, Rubiyah MH, Joy J, Moores A, Drisko GL, Sanchez C (2018) Nanocellulose, a versatile green platform: from biosources to materials and their applications. *Chem Rev* 118(24):11575–11625. <https://doi.org/10.1021/acs.chemrev.7b00627>
2. Mohanty AK, Wibowo A, Misra M, Drzal LT (2004) Effect of process engineering on the performance of natural fiber reinforced cellulose acetate biocomposites. *Composites A* 35(3):363–370. <https://doi.org/10.1016/j.compositesa.2003.09.015>
3. Lundquist L, Marque B, Hagstrand PO, Leterrier Y, Månson JAE (2003) Novel pulp fibre reinforced thermoplastic composites. *Compos Sci Technol* 63(1):137–152. [https://doi.org/10.1016/S0266-3538\(02\)00192-6](https://doi.org/10.1016/S0266-3538(02)00192-6)
4. Kim J-P, Yoon T-H, Mun S-P, Rhee J-M, Lee J-S (2006) Wood-polyethylene composites using ethylene-vinyl alcohol copolymer as adhesion promoter. *Bioresour Technol* 97(3):494–499. <https://doi.org/10.1016/j.biortech.2005.02.048>
5. Bismarck A, Baltazar-Y-Jimenez A, Sarikakis K (2006) Green composites as panacea? Socio-economic aspects of green materials. *Environ Dev Sustain* 8(3):445–463. <https://doi.org/10.1007/s10668-005-8506-5>
6. Park D, Yun Y-S, Park JM (2010) The past, present, and future trends of biosorption. *Biotechnol Bioprocess Eng* 15(1):86–102. <https://doi.org/10.1007/s12257-009-0199-4>
7. Singh S, Kumar V, Datta S, Dhanjal DS, Sharma K, Samuel J, Singh J (2020) Current advancement and future prospect of biosorbents for bioremediation. *Sci Total Environ* 709:135895. <https://doi.org/10.1016/j.scitotenv.2019.135895>
8. Ahmad R, Hamid R, Osman SA (2019) Physical and chemical modifications of plant fibres for reinforcement in cementitious composites. *Adv Civil Eng* 2019:5185806. <https://doi.org/10.1155/2019/5185806>
9. Thakur VK, Thakur MK, Gupta RK (2013) Rapid synthesis of graft copolymers from natural cellulose fibers. *Carbohydr Polym* 98(1):820–828. <https://doi.org/10.1016/j.carbpol.2013.06.072>
10. Kaith B, Kalia S (2007) Grafting of flax fiber (*Linum usitatissimum*) with vinyl monomers for enhancement of properties of flax-phenolic composites. *Polym J* 39(12):1319–1327. <https://doi.org/10.1295/polymj.PJ2007073>
11. Thakur VK, Thakur MK, Gupta RK (2014) Graft copolymers of natural fibers for green composites. *Carbohydr Polym* 104:87–93. <https://doi.org/10.1016/j.carbpol.2014.01.016>
12. Wojnárovits L, Földvály CM, Takács E (2010) Radiation-induced grafting of cellulose for adsorption of hazardous water pollutants: a review. *Radiat Phys Chem* 79(8):848–862. <https://doi.org/10.1016/j.radphyschem.2010.02.006>
13. Kumar D, Pandey J, Raj V, Kumar P (2017) A review on the modification of polysaccharide through graft copolymerization for various potential applications. *Open Med Chem J* 11:109–126. <https://doi.org/10.2174/1874104501711010109>
14. Komuraiah A, Kumar NS, Prasad BD (2014) Chemical composition of natural fibers and its influence on their mechanical properties. *Mech Compos Mater* 50(3):359–376. <https://doi.org/10.1007/s11029-014-9422-2>
15. Akin DE (2010) Flax—structure, chemistry, retting and processing. *Industrial applications of natural fibres*. Wiley, Chichester, pp 87–108. <https://doi.org/10.1002/9780470660324.ch4>
16. Madhu P, Sanjay MR, Sentharamaikkannan P, Pradeep S, Saravanakumar SS, Yogesha B (2019) A review on synthesis and characterization of commercially available natural fibers: part

- II. *J Nat Fibers* 16(1):25–36. <https://doi.org/10.1080/15440478.2017.1379045>
17. Baiardo M, Frisoni G, Scandola M, Licciardello A (2002) Surface chemical modification of natural cellulose fibers. *J Appl Polym Sci* 83(1):38–45. <https://doi.org/10.1002/app.2229>
  18. Mahjoub R, Yatim JM, Mohd Sam AR, Hashemi SH (2014) Tensile properties of kenaf fiber due to various conditions of chemical fiber surface modifications. *Constr Build Mater* 55:103–113. <https://doi.org/10.1016/j.conbuildmat.2014.01.036>
  19. Varghese AM, Mittal V (2018) Surface modification of natural fibers. In: Shimpi NG (ed) *Biodegradable and biocompatible polymer composites*. Woodhead Publishing, Cambridge, pp 115–155. <https://doi.org/10.1016/B978-0-08-100970-3.00005-5>
  20. Xie Y, Hill CAS, Xiao Z, Militz H, Mai C (2010) Silane coupling agents used for natural fiber/polymer composites: a review. *Composites A* 41(7):806–819. <https://doi.org/10.1016/j.compositesa.2010.03.005>
  21. Akil H, Omar M, Mazuki A, Safiee S, Ishak ZM, Bakar AA (2011) Kenaf fiber reinforced composites: a review. *Mater Des* 32(8–9):4107–4121. <https://doi.org/10.1016/j.matdes.2011.04.008>
  22. Fuqua MA, Huo S, Ulven CA (2012) Natural fiber reinforced composites. *Polym Rev* 52(3):259–320. <https://doi.org/10.1080/15583724.2012.705409>
  23. Peças P, Carvalho H, Salman H, Leite M (2018) Natural fibre composites and their applications: a review. *J Compos Sci*. <https://doi.org/10.3390/jcs2040066>
  24. Sepe R, Bollino F, Boccarusso L, Caputo F (2018) Influence of chemical treatments on mechanical properties of hemp fiber reinforced composites. *Composites B* 133:210–217. <https://doi.org/10.1016/j.compositesb.2017.09.030>
  25. Yildizhan S, Çalik A, Ozcanli M (2018) Serin H Bio-composite materials: a short review of recent trends, mechanical and chemical properties, and applications. *Eur Mech Sci*. <https://doi.org/10.26701/EMS.369005>
  26. Zwawi M (2021) A review on natural fiber bio-composites, surface modifications and applications. *Molecules* 26(2):404. <https://doi.org/10.3390/molecules26020404>
  27. Kumar R, Sharma RK, Singh AP (2018) Grafted cellulose: a bio-based polymer for durable applications. *Polym Bull* 75(5):2213–2242. <https://doi.org/10.1007/s00289-017-2136-6>
  28. Harris JA, Arthur JC Jr, Goynes WR Jr (1979) Flame resistant cotton fabrics prepared by radiation-initiated polymerization with vinyl phosphonate oligomer and N-methylolacrylamide. *J Appl Polym Sci* 23(9):2555–2565. <https://doi.org/10.1002/app.1979.070230902>
  29. Shavandi A, Ali MA (2019) Graft polymerization onto wool fibre for improved functionality. *Prog Org Coat* 130:182–199. <https://doi.org/10.1016/j.porgcoat.2019.01.054>
  30. Ramamoorthy SK, Skrifvars M, Persson A (2015) A review of natural fibers used in biocomposites: plant, animal and regenerated cellulose fibers. *Polym Rev* 55(1):107–162. <https://doi.org/10.1080/15583724.2014.971124>
  31. Sfiligoj Smole M, Hribernik S, Stana Kleinschek K, Kreže T (2013) Plant fibres for textile and technical applications. *Adv Agrophys Res*. <https://doi.org/10.1016/j.porgcoat.2019.01.054>
  32. Karger-Kocsis J, Mahmood H, Pegoretti A (2015) Recent advances in fiber/matrix interphase engineering for polymer composites. *Prog Mater Sci* 73:1–43. <https://doi.org/10.1016/j.pmatsci.2015.02.003>
  33. Klemm D, Heublein B, Fink H-P, Bohn A (2005) Cellulose: fascinating biopolymer and sustainable raw material. *Angew Chem Int Ed* 44(22):3358–3393. <https://doi.org/10.1002/anie.200460587>
  34. Hiraishi K, Takeda Y, Shiobara N, Shibusawa H, Jimma F, Kashiwagi N, Saniabadi AR, Adachi M (2003) Studies on the mechanisms of leukocyte adhesion to cellulose acetate beads: an in vitro model to assess the efficacy of cellulose acetate carrier-based granulocyte and monocyte adsorptive apheresis. *Ther Apher Dial* 7(3):334–340. <https://doi.org/10.1046/j.1526-0968.2003.00049.x>
  35. Seavey KC, Ghosh I, Davis RM, Glasser WG (2001) Continuous cellulose fiber-reinforced cellulose ester composites. I. Manufacturing options. *Cellulose* 8(2):149–159. <https://doi.org/10.1023/A:1016713131851>
  36. Tomšič B, Simončič B, Orel B, Černe L, Tavčer PF, Zorko M, Jerman I, Vilčnik A, Kovač J (2008) Sol–gel coating of cellulose fibres with antimicrobial and repellent properties. *J Sol-Gel Sci Technol* 47(1):44–57. <https://doi.org/10.1007/s10971-008-1732-1>
  37. Dellal G, Soylemezoglu F, Erdogan Z, Pehlivan E, Köksal Ö, Tuncer SS (2014) Present situation and future of animal fiber production in turkey: a review. *J Life Sci* 8:192–200
  38. Tavares TD, Antunes JC, Ferreira F, Felgueiras HP (2020) Bio-functionalization of natural fiber-reinforced biocomposites for biomedical applications. *Biomolecules* 10(1):148. <https://doi.org/10.3390/biom10010148>
  39. Cruz J, Fanguero R (2016) Surface modification of natural fibers: a review. *Proced Eng* 155:285–288. <https://doi.org/10.1016/j.proeng.2016.08.030>
  40. Mohanty AK, Misra M, Drzal LT (2001) Surface modifications of natural fibers and performance of the resulting biocomposites: an overview. *Compos Interfaces* 8(5):313–343. <https://doi.org/10.1163/156855401753255422>
  41. Wei L, McDonald AG (2016) A review on grafting of biofibers for biocomposites. *Materials (Basel)* 9(4):303. <https://doi.org/10.3390/ma9040303>
  42. Kang PH, Jeun JP, Chung BY, Kim JS, Nho YC (2007) Preparation and characterization of glycidyl methacrylate (GMA) grafted kapok fiber by using radiation induced-grafting technique. *J Ind Eng Chem* 13(6):956–958
  43. Okieimen EF, Ebhoaye JE (1986) Grafting acrylonitrile and acrylic acid monomers on cellulosic materials. *J Appl Polym Sci* 31(5):1275–1280. <https://doi.org/10.1002/app.1986.070310513>
  44. Nasef MM, Hegazy E-SA (2004) Preparation and applications of ion exchange membranes by radiation-induced graft copolymerization of polar monomers onto non-polar films. *Prog Polym Sci* 29(6):499–561. <https://doi.org/10.1016/j.progpolymsci.2004.01.003>
  45. Taghizadeh MT, Mehrdad A (2006) Kinetic study of graft polymerization of acrylic acid and ethyl methacrylate onto starch by ceric ammonium nitrate. *Iran J Chem Chem Eng (IJCCCE)* 25(1):1–12. <https://doi.org/10.30492/IJCCCE.2006.7792>
  46. Biçak N, Sherrington DC, Senkal BF (1999) Graft copolymer of acrylamide onto cellulose as mercury selective sorbent. *React Funct Polym* 41(1):69–76. [https://doi.org/10.1016/S1381-5148\(99\)00021-8](https://doi.org/10.1016/S1381-5148(99)00021-8)
  47. Ibrahim MM, Fiefel EM, El-Zawawy WK (2002) Cellulose membranes grafted with vinyl monomers in a homogeneous system. *Polym Adv Technol* 13(7):548–557. <https://doi.org/10.1002/pat.224>
  48. Ogiwara Y, Ogiwara Y, Kubota H (1968) Studies of the initiation mechanism of ferric ion–hydrogen peroxide systems in graft copolymerization on cellulose. *J Appl Polym Sci* 12(12):2575–2584. <https://doi.org/10.1002/app.1968.070121201>
  49. Gupta KC, Sahoo S (2001) Co(III) acetylacetonate-complex-initiated grafting of N-vinyl pyrrolidone on cellulose in aqueous media. *J Appl Polym Sci* 81(9):2286–2296. <https://doi.org/10.1002/app.1669>



50. Ouajai S, Hodzic A, Shanks R (2004) Morphological and grafting modification of natural cellulose fibers. *J Appl Polym Sci* 94(6):2456–2465. <https://doi.org/10.1002/app.21191>
51. Bardhan K, Mukhopadhyay S, Chatterjee SR (1977) Grafting of acrylamide onto methyl cellulose by persulfate ion. *J Polym Sci: Polym Chem Ed* 15(1):141–148. <https://doi.org/10.1002/pol.1977.170150114>
52. Abdel-Razik EA (1990) Homogeneous graft copolymerization of acrylamide onto ethylcellulose. *Polymer* 31(9):1739–1744. [https://doi.org/10.1016/0032-3861\(90\)90195-5](https://doi.org/10.1016/0032-3861(90)90195-5)
53. Naguib HF (2002) Chemically induced graft copolymerization of itaconic acid onto sisal fibers. *J Polym Res* 9(3):207–211. <https://doi.org/10.1023/A:1021399826969>
54. Sabaa MW, Mokhtar SM (2002) Chemically induced graft copolymerization of itaconic acid onto cellulose fibers. *Polym Test* 21(3):337–343. [https://doi.org/10.1016/S0142-9418\(01\)00094-0](https://doi.org/10.1016/S0142-9418(01)00094-0)
55. Zhou Y, Zhang M, Hu X, Wang X, Niu J, Ma T (2013) Adsorption of cationic dyes on a cellulose-based multicarboxyl adsorbent. *J Chem Eng Data* 58(2):413–421. <https://doi.org/10.1021/jc301140c>
56. Mishra S, Misra M, Tripathy SS, Nayak SK, Mohanty AK (2001) Graft copolymerization of acrylonitrile on chemically modified sisal fibers. *Macromol Mater Eng* 286(2):107–113. [https://doi.org/10.1002/1439-2054\(20010201\)286:2](https://doi.org/10.1002/1439-2054(20010201)286:2)
57. Pulat M, Isakoca C (2006) Chemically induced graft copolymerization of vinyl monomers onto cotton fibers. *J Appl Polym Sci* 100(3):2343–2347. <https://doi.org/10.1002/app.23060>
58. Mondal MIH, Haque MM-U (2007) Effect of grafting methacrylate monomers onto jute constituents with a potassium persulfate initiator catalyzed by Fe(II). *J Appl Polym Sci* 103(4):2369–2375. <https://doi.org/10.1002/app.25276>
59. Mondal MIH (2013) Grafting of methyl acrylate and methyl methacrylate onto jute fiber: Physico-chemical characteristics of the grafted jute. *J Eng Fibers Fabr* 8(3):155892501300800320. <https://doi.org/10.1177/155892501300800305>
60. Barsbay M, Güven O, Stenzel MH, Davis TP, Barner-Kowollik C, Barner L (2007) Verification of controlled grafting of styrene from cellulose via radiation-induced RAFT polymerization. *Macromolecules* 40(20):7140–7147. <https://doi.org/10.1021/ma070825u>
61. Mondal MIH, Khan MMR, Islam MM, Islam MS, Rabbi MA (2016) Characterization of grafted jute fiber using acrylate monomers pretreated with alkali. *Fash Text* 3(1):9. <https://doi.org/10.1186/s40691-016-0060-2>
62. Sharma Rajeev K, Sunil K (2013) Graft copolymerization of binary monomer mixtures onto silk fibre. *Res J Chem Sci* 11:73–81
63. Nasef MM (2014) Radiation-grafted membranes for polymer electrolyte fuel cells: current trends and future directions. *Chem Rev* 114(24):12278–12329. <https://doi.org/10.1021/cr4005499>
64. Nasef MM, Güven O (2012) Radiation-grafted copolymers for separation and purification purposes: Status, challenges and future directions. *Prog Polym Sci* 37(12):1597–1656. <https://doi.org/10.1016/j.progpolymsci.2012.07.004>
65. Moawia RM, Nasef MM, Mohamed NH, Ripin A (2016) Modification of flax fibres by radiation induced emulsion graft copolymerization of glycidyl methacrylate. *Radiat Phys Chem* 122:35–42. <https://doi.org/10.1016/j.radphyschem.2016.01.008>
66. Dorschner H, Lappan U, Lunkwitz K (1998) Electron beam facility in polymer research: radiation induced functionalization of polytetrafluoroethylene. *Nucl Instrum Methods Phys Res B* 139(1):495–501. [https://doi.org/10.1016/S0168-583X\(97\)00937-3](https://doi.org/10.1016/S0168-583X(97)00937-3)
67. Le Moigne N, Sonnier R, El Hage R, Rouif S (2017) Radiation-induced modifications in natural fibres and their biocomposites: opportunities for controlled physico-chemical modification pathways? *Ind Crops Prod* 109:199–213. <https://doi.org/10.1016/j.indcrop.2017.08.027>
68. Khan MA, Rahaman MS, Al-Jubayer A, Islam J (2015) Modification of jute fibers by radiation-induced graft copolymerization and their applications. In: Thakur VK (ed) *Cellulose-based graft copolymers: structure and chemistry*. CRC Press, Boca Raton, pp 209–235
69. Mokhtar SM, Mostapha TB, Sabaa MW (2002)  $\gamma$ -Radiation induced graft copolymerization of N-phenyl- and N-p-hydroxyphenyl maleimide onto cotton fabrics. *Polym-Plast Technol Eng* 41(1):183–197. <https://doi.org/10.1081/PPT-120002069>
70. Khan F (2005) Characterization of methyl methacrylate grafting onto preirradiated biodegradable lignocellulose fiber by  $\gamma$ -radiation. *Macromol Biosci* 5(1):78–89. <https://doi.org/10.1002/mabi.200400137>
71. Sharif J, Mohamad SF, Othman NAF, Bakaruddin NA, Osman HN, Güven O (2013) Graft copolymerization of glycidyl methacrylate onto delignified kenaf fibers through pre-irradiation technique. *Radiat Phys Chem* 91:125–131. <https://doi.org/10.1016/j.radphyschem.2013.05.035>
72. El-Mosallamy E-SH (2001) Improved dyeability and mechanical properties of wool fibers grafted with poly(acrylic acid) by gamma-radiation. *J Macromol Sci A* 38(11):1167–1174. <https://doi.org/10.1081/MA-100107136>
73. Barsbay M, Güven O, Davis TP, Barner-Kowollik C, Barner L (2009) RAFT-mediated polymerization and grafting of sodium 4-styrenesulfonate from cellulose initiated via  $\gamma$ -radiation. *Polymer* 50(4):973–982. <https://doi.org/10.1016/j.polymer.2008.12.027>
74. Kang H, Liu R, Huang Y (2015) Graft modification of cellulose: methods, properties and applications. *Polymer* 70:A1–A16. <https://doi.org/10.1016/j.polymer.2015.05.041>
75. Bhosale RR, Gangadharappa HV, Moin A, Gowda DV, Osmani RAM (2015) A review on grafting modification of polysaccharides by microwave irradiation—distinctive practice for application in drug delivery. *Int J Curr Pharm Rev Res* 6(1):8–17
76. Kaur L, Gupta G (2017) A review on microwave assisted grafting of polymers. *Int J Pharm Sci Res* 8(2):422. [https://doi.org/10.13040/IJPSR.0975-8232.8\(2\).422-26](https://doi.org/10.13040/IJPSR.0975-8232.8(2).422-26)
77. Kalia S, Sabaa MW, Kango S (2013) Polymer grafting: a versatile means to modify the polysaccharides. In: Kalia S, Sabaa MW (eds) *Polysaccharide based graft copolymers*. Springer, Berlin, pp 1–14. [https://doi.org/10.1007/978-3-642-36566-9\\_1](https://doi.org/10.1007/978-3-642-36566-9_1)
78. Singh V, Kumar P, Sanghi R (2012) Use of microwave irradiation in the grafting modification of the polysaccharides—a review. *Prog Polym Sci* 37(2):340–364. <https://doi.org/10.1016/j.progpolymsci.2011.07.005>
79. Zhao B-X, Wang P, Zheng T, Shu J (2005) Preparation of high water-absorbent resin with cellulose under microwave radiation and its performances. *Mater Sci Eng* 21(4):133
80. Shu J, Li XJ, Zhao DB (2011) Microwave-irradiated preparation of super absorbent resin by graft copolymerization of cellulose and acrylic acid/acrylamide. *Adv Mater Res*. <https://doi.org/10.4028/www.scientific.net/AMR.148-149.799>
81. Feng H, Li J, Wang L (2010) Preparation of biodegradable flax shive cellulose-based superabsorbent polymer under microwave irradiation. *BioResources* 5(3):12
82. Gupta VK, Pathania D, Priya B, Singha AS, Sharma G (2014) Microwave induced synthesis of graft copolymer of binary vinyl monomer mixtures onto delignified *Grewia optiva* fiber: application in dye removal. *Front Chem*. <https://doi.org/10.3389/fchem.2014.00059>
83. Singha AS, Guleria A, Rana RK (2013) Ascorbic acid/H<sub>2</sub>O<sub>2</sub>-initiated graft copolymerization of methyl methacrylate onto *Abelmoschus Esculentus* fiber: a kinetic approach. *Int J Polym*

- Anal Charact 18(1):1–14. <https://doi.org/10.1080/1023666X.2012.723852>
84. Kaith B, Kalia S (2008) Graft copolymerization of MMA onto flax under different reaction conditions: a comparative study. *Express Polym Lett* 2(2):93–100. <https://doi.org/10.3144/expresspolymlett.2008.13>
  85. Kaith B, Kalia S (2008) Preparation of microwave radiation induced graft copolymers and their applications as reinforcing material in phenolic composites. *Polym Compos* 29(7):791–797. <https://doi.org/10.1002/pc.20445>
  86. Singha AS, Rana RK (2010) Microwave induced graft copolymerization of methyl methacrylate onto lignocellulosic fibers. *Int J Polym Anal Charact* 15(6):370–386. <https://doi.org/10.1080/1023666X.2010.500539>
  87. Kapoor H, Singha AS, Kapoor M (2016) Microwave radiation induced surface modification of silk fibers with methylmethacrylate and acrylonitrile monomers through graft-copolymerization. *J Chem Pharm Res* 8(8):212–217
  88. Kumar D, Pandey J, Kumar P (2018) Microwave assisted synthesis of binary grafted psyllium and its utility in anticancer formulation. *Carbohydr Polym* 179:408–414. <https://doi.org/10.1016/j.carbpol.2017.09.093>
  89. Sangermano M, Razza N (2019) Light induced grafting-from strategies as powerful tool for surface modification. *Express Polym Lett* 13(2):135. <https://doi.org/10.3144/expresspolymlett.2019.13>
  90. Ghosh P, Paul SK (1983) Photograft copolymerization of methyl methacrylate (MMA) on bleached jute fiber using ferric sulfate,  $\text{Fe}_2(\text{SO}_4)_3$ , as initiator in limited aqueous system. *J Macromol Sci A* 20(2):169–178. <https://doi.org/10.1080/00222338308069957>
  91. Khan F (2004) Photoinduced graft-copolymer synthesis and characterization of methacrylic acid onto natural biodegradable lignocellulose fiber. *Biomacromol* 5(3):1078–1088. <https://doi.org/10.1021/bm049967b>
  92. Khan MA, Majumder SC, Arifur Rahman M, Noor FG, Zaman HU, Mollah MZI, Khan RA, Das LR (2010) Mechanical and electrical properties of photocured jute fabric with 2-hydroxy ethylacrylate. *Fibers Polym* 11(3):391–397. <https://doi.org/10.1007/s12221-010-0391-3>
  93. Kianfar P, Abate MT, Trovato V, Rosace G, Ferri A, Bongiovanni R, Vitale A (2020) Surface functionalization of cotton fabrics by photo-grafting for Ph sensing applications. *Front Mater*. <https://doi.org/10.3389/fmats.2020.00039>
  94. Morent R, De Geyter N, Verschuren J, De Clerck K, Kiekens P, Lays C (2008) Non-thermal plasma treatment of textiles. *Surf Coat Technol* 202(14):3427–3449. <https://doi.org/10.1016/j.surfcoat.2007.12.027>
  95. Kale KH, Desai A (2011) Atmospheric pressure plasma treatment of textiles using non-polymerising gases. *Indian J Fibre Text Res* 36:289–299
  96. Dénes F, Macoveanu MM, Negulescu I (1984) Surface modification and grafting of natural and synthetic fibres and fabrics under cold plasma conditions. *Die Makromolekulare Chemie: Macromolecular Chemistry and Physics* 8(S19841):17–36. <https://doi.org/10.1002/macp.1984.020081984103>
  97. Kalia S, Thakur K, Celli A, Kiechel MA, Schauer CL (2013) Surface modification of plant fibers using environment friendly methods for their application in polymer composites, textile industry and antimicrobial activities: a review. *J Environ Chem Eng* 1(3):97–112. <https://doi.org/10.1016/j.jece.2013.04.009>
  98. Zubaidi HT (1996) Graft polymerization of hydrophilic monomers onto textile fibers treated by glow discharge plasma. *J Appl Polym Sci* 61(9):1579–1584. [https://doi.org/10.1002/\(SICI\)1097-4628\(19960829\)61:9](https://doi.org/10.1002/(SICI)1097-4628(19960829)61:9)
  99. Tsafack MJ, Levalois-Grützmacher J (2006) Flame retardancy of cotton textiles by plasma-induced graft-polymerization (PIGP). *Surf Coat Technol* 201(6):2599–2610. <https://doi.org/10.1016/j.surfcoat.2006.05.002>
  100. Boonyawan D (2012) Atmospheric pressure plasma jet induced graft-polymerization for flame retardant silk. *Adv Plasma Spray Appl*. <https://doi.org/10.5772/28047>
  101. Malshe P, Mazlumpour M, El-Shafei A, Hauser P (2012) Functional military textile: plasma-induced graft polymerization of DADMAC for antimicrobial treatment on nylon-cotton blend fabric. *Plasma Chem Plasma Process* 32(4):833–843. <https://doi.org/10.1007/s11090-012-9380-1>
  102. Helmy HM, Hauser P, El-Shafei A (2017) Influence of atmospheric plasma-induced graft polymerization of DADMAC into cotton on dyeing with acid dyes. *J Text Inst* 108(11):1871–1878. <https://doi.org/10.1080/00405000.2017.1298206>
  103. Sekine A, Seko N, Tamada M, Suzuki Y (2010) Biodegradable metal adsorbent synthesized by graft polymerization onto non-woven cotton fabric. *Radiat Phys Chem* 79(1):16–21. <https://doi.org/10.1016/j.radphyschem.2009.08.007>
  104. Rangabhashiyam S, Anu N, Selvaraju N (2013) Sequestration of dye from textile industry wastewater using agricultural waste products as adsorbents. *J Environ Chem Eng* 1(4):629–641. <https://doi.org/10.1016/j.jece.2013.07.014>
  105. Ayangbenro AS, Babalola OO (2017) A new strategy for heavy metal polluted environments: a review of microbial biosorbents. *Int J Environ Res Public Health*. <https://doi.org/10.3390/ijerph141010094>
  106. Khademian E, Salehi E, Sanaeepur H, Galiano F, Figoli A (2021) A systematic review on carbohydrate biopolymers for adsorptive remediation of copper ions from aqueous environments—part B: isotherms, thermokinetics and reusability. *Sci Total Environ* 754:142048. <https://doi.org/10.1016/j.scitotenv.2020.142048>
  107. Khademian E, Salehi E, Sanaeepur H, Galiano F, Figoli A (2020) A systematic review on carbohydrate biopolymers for adsorptive remediation of copper ions from aqueous environments—part A: classification and modification strategies. *Sci Total Environ* 738:139829. <https://doi.org/10.1016/j.scitotenv.2020.139829>
  108. Na Y, Lee J, Lee SH, Kumar P, Kim JH, Patel R (2020) Removal of heavy metals by polysaccharide: a review. *Polym-Plast Technol Mater* 59(16):1770–1790. <https://doi.org/10.1080/25740881.2020.1768545>
  109. Ting TM, Nasef MM (2017) Modification of polyethylene-polypropylene fibers by emulsion and solvent radiation grafting systems for boron removal. *Fibers Polym* 18(6):1048–1055. <https://doi.org/10.1007/s12221-017-6840-5>
  110. Hubbe MA, Hasan SH, Ducoste JJ (2011) Cellulosic substrates for removal of pollutants from aqueous systems: a review. 1. Metals. *BioResources* 6(2):2161–2287. <https://doi.org/10.15376/biores.6.2.2161-2287>
  111. Crini G, Lichtfouse E, Wilson LD, Morin-Crini N (2019) Conventional and non-conventional adsorbents for wastewater treatment. *Environ Chem Lett* 17(1):195–213. <https://doi.org/10.1007/s10311-018-0786-8>
  112. Abdel-Aal SE, Gad YH, Dessouki AM (2006) The use of wood pulp and radiation-modified starch in wastewater treatment. *J Appl Polym Sci* 99(5):2460–2469. <https://doi.org/10.1002/app.22801>
  113. Hassan MS, Zohdy MH (2018) Adsorption kinetics of toxic heavy metal ions from aqueous solutions onto grafted jute fibers with acrylic acid by gamma irradiation. *J Nat Fibers* 15(4):506–516. <https://doi.org/10.1080/15440478.2017.1330721>
  114. Hassan MS, Zohdy MH (2018) Removal of toxic heavy metal ions from aqueous solutions using jute fibers grafted with acrylic acid by gamma irradiation. *J Vinyl Add Tech* 24(4):339–346. <https://doi.org/10.1002/vnl.21603>
  115. Bao-Xiu Z, Peng W, Tong Z, Chun-yun C, Jing S (2006) Preparation and adsorption performance of a cellulosic-adsorbent resin

- for copper (II). *J Appl Polym Sci* 99(6):2951–2956. <https://doi.org/10.1002/app.22986>
116. Kamel S, Hassan E, El-Sakhawy M (2006) Preparation and application of acrylonitrile-grafted cyanoethyl cellulose for the removal of copper (II) ions. *J Appl Polym Sci* 100(1):329–334. <https://doi.org/10.1002/app.23317>
  117. Singha AS, Guleria A (2015) Synthesis and applications of functional polymers from natural okra fibers for removal of Cu(II) ions from aqueous solution. *J Nat Fibers* 12(6):587–603. <https://doi.org/10.1080/15440478.2014.984049>
  118. Madrid JF, Nuesca GM, Abad LV (2013) Gamma radiation-induced grafting of glycidyl methacrylate (GMA) onto water hyacinth fibers. *Radiat Phys Chem* 85:182–188. <https://doi.org/10.1016/j.radphyschem.2012.10.006>
  119. Madrid JF, Nuesca GM, Abad LV (2014) Amine functionalized radiation-induced grafted water hyacinth fibers for Pb<sup>2+</sup>, Cu<sup>2+</sup> and Cr<sup>3+</sup> uptake. *Radiat Phys Chem* 97:246–252. <https://doi.org/10.1016/j.radphyschem.2013.12.009>
  120. Madrid JF, Cabalar PJE, Abad LV (2018) Radiation-induced graft polymerization of acrylic acid and glycidyl methacrylate onto abaca/polyester nonwoven fabric. *J Nat Fibers* 15(5):625–638. <https://doi.org/10.1080/15440478.2017.1349713>
  121. Hebeish A, Elnagar K, Helal M, Ragab M, Shaaban M (2014) UV/O<sub>3</sub> preirradiated cotton fabric-containing chitosan for effective removal of heavy metals. *Mater Sci Appl* 5(10):698. <https://doi.org/10.4236/msa.2014.510071>
  122. Sokker HH, Badawy SM, Zayed EM, Nour Eldien FA, Farag AM (2009) Radiation-induced grafting of glycidyl methacrylate onto cotton fabric waste and its modification for anchoring hazardous wastes from their solutions. *J Hazard Mater* 168(1):137–144. <https://doi.org/10.1016/j.jhazmat.2009.02.039>
  123. Sun Z, Liu Y, Huang Y, Tan X, Zeng G, Hu X, Yang Z (2014) Fast adsorption of Cd<sup>2+</sup> and Pb<sup>2+</sup> by EGTA dianhydride (EGTAD) modified ramie fiber. *J Colloid Interface Sci* 434:152–158. <https://doi.org/10.1016/j.jcis.2014.07.036>
  124. Adewuyi A, Pereira FV (2017) Chemical modification of cellulose isolated from underutilized hibiscus sabdariffa via surface grafting: a potential bio-based resource for industrial application. *J Chem Chem Eng* 66(7–8):327–338. <https://doi.org/10.15255/KUI.2016.024>
  125. Kumar R, Sharma RK, Singh AP (2019) Synthesis and characterization of cellulose based graft copolymers with binary vinyl monomers for efficient removal of cationic dyes and Pb(II) ions. *J Polym Res* 26(6):135. <https://doi.org/10.1007/s10965-019-1790-9>
  126. Monier M, Nawar N, Abdel-Latif DA (2010) Preparation and characterization of chelating fibers based on natural wool for removal of Hg(II), Cu(II) and Co(II) metal ions from aqueous solutions. *J Hazard Mater* 184(1):118–125. <https://doi.org/10.1016/j.jhazmat.2010.08.013>
  127. Monier M, Ayad DM, Sarhan AA (2010) Adsorption of Cu(II), Hg(II), and Ni(II) ions by modified natural wool chelating fibers. *J Hazard Mater* 176(1):348–355. <https://doi.org/10.1016/j.jhazmat.2009.11.034>
  128. Wang F, Zheng Y, Zhu Y, Wang A (2016) Oriented functionalization of natural hollow kapok fiber for highly efficient removal of toxic Hg(II) from aqueous solution. *Front Environ Sci*. <https://doi.org/10.3389/fenvs.2016.00004>
  129. Kumar D, Pandey J, Khan N, Kumar P, Kundu PP (2019) Synthesize and characterization of binary grafted psyllium for removing toxic mercury (II) ions from aqueous solution. *Mater Sci Eng C* 104:109900. <https://doi.org/10.1016/j.msec.2019.109900>
  130. Cao C, Kang H, Che N, Liu Z, Li P, Zhang C, Li W, Liu R, Huang Y (2014) Wool graft polyacrylamidoxime as the adsorbent for both cationic and anionic toxic ions from aqueous solutions. *RSC Adv* 4(105):60609–60616. <https://doi.org/10.1039/C4RA10514A>
  131. Hassan MS, Ali NM, Attia RM, Zohdy MH, Rabie AM (2015) Adsorption of heavy metal ions from aqueous media using amidoximated jute fibres: a comparative study. *Egypt J Radiat Sci Appl* 28(1):61–75. <https://doi.org/10.21608/ejrsa.2015.1534>
  132. Duranoğlu D, Buyruklardan Kaya İG, Beker U, Şenkal BF (2012) Synthesis and adsorption properties of polymeric and polymer-based hybrid adsorbent for hexavalent chromium removal. *Chem Eng J* 181–182:103–112. <https://doi.org/10.1016/j.cej.2011.11.028>
  133. Hajeeth T, Sudha PN, Vijayalakshmi K, Gomathi T (2014) Sorption studies on Cr (VI) removal from aqueous solution using cellulose grafted with acrylonitrile monomer. *Int J Biol Macromol* 66:295–301. <https://doi.org/10.1016/j.ijbiomac.2014.02.027>
  134. Hoshina H, Takahashi M, Kasai N, Seko N (2012) Adsorbent for arsenic (V) removal synthesized by radiation-induced graft polymerization onto nonwoven cotton fabric. *Int J Org Chem* 2(2):173–177. <https://doi.org/10.4236/ijoc.2012.23026>
  135. Madrid JF, Ueki Y, Seko N (2013) Abaca/polyester nonwoven fabric functionalization for metal ion adsorbent synthesis via electron beam-induced emulsion grafting. *Radiat Phys Chem* 90:104–110. <https://doi.org/10.1016/j.radphyschem.2013.05.004>
  136. Ajitha P, Vijayalakshmi K, Saranya M, Gomathi T, Rani K, Sudha PN, Sukumaran A (2017) Removal of toxic heavy metal lead (II) using chitosan oligosaccharide-graft-maleic anhydride/polyvinyl alcohol/silk fibroin composite. *Int J Biol Macromol* 104:1469–1482. <https://doi.org/10.1016/j.ijbiomac.2017.05.111>
  137. Zang C, Zhang D, Xiong J, Lin H, Chen Y (2014) Preparation of a novel adsorbent and heavy metal ion adsorption. *J Eng Fibers Fabr* 9(4):155892501400900400. <https://doi.org/10.1177/155892501400900420>
  138. Zamarripa-Cerón JL, García-Cruz JC, Martínez-Arellano AC, Castro-Guerrero CF, Ángeles-San Martín ME, Morales-Cepeda AB (2016) Heavy metal removal using hydroxypropyl cellulose and polyacrylamide gels, kinetic study. *J Appl Polym Sci*. <https://doi.org/10.1002/app.43285>
  139. Hossain MM, Moniruzzaman M, Khan MA, Shahjahan M, Alam MZ, Jamal MS (2014) Preparation of selective ion adsorbent by gamma radiation induced graft copolymerization of n-butyl methacrylate & phosphoric acid on jute fiber. *Indian J Adv Chem Sci* 2(2):146–150
  140. Rahman ML, Sarkar SM, Yusoff MM, Abdullah MH (2016) Efficient removal of transition metal ions using poly(amidoxime) ligand from polymer grafted kenaf cellulose. *RSC Adv* 6(1):745–757. <https://doi.org/10.1039/C5RA18502E>
  141. Gupta VK, Agarwal S, Singh P, Pathania D (2013) Acrylic acid grafted cellulosic *Luffa cylindrical* fiber for the removal of dye and metal ions. *Carbohydr Polym* 98(1):1214–1221. <https://doi.org/10.1016/j.carbpol.2013.07.019>
  142. Velusamy S, Roy A, Sundaram S, Kumar Mallick T (2021) A review on heavy metal ions and containing dyes removal through graphene oxide-based adsorption strategies for textile wastewater treatment. *Chem Rec (New York, NY)*. <https://doi.org/10.1002/ctr.202000153>
  143. Hubbe M, Beck K, O'Neal W, Sharma YC (2012) Cellulosic substrates for removal of pollutants from aqueous systems: a review. 2. Dyes. *BioResources* 7(2):2592–2687. <https://doi.org/10.15376/biores.7.2.2592-2687>
  144. Dafader N, Rahman N, Alam M (2014) Study on grafting of acrylic acid onto cotton using gamma radiation and its application as dye adsorbent. *Nucl Sci Appl* 23(1 & 2):37–40
  145. Peng B, Yao Z, Wang X, Crombeen M, Sweeney DG, Tam KC (2020) Cellulose-based materials in wastewater treatment of petroleum industry. *Green Energy Environ* 5(1):37–49. <https://doi.org/10.1016/j.gee.2019.09.003>
  146. Hashem A, Sokker H, Halim EA, Gamal A (2005)  $\gamma$ -induced graft copolymerization onto cellulosic fabric waste for cationic

- dye removal. *Adsorpt Sci Technol* 23(6):455–466. <https://doi.org/10.1260/026361705774859901>
147. Abdel-Halim ES, Al-Hoqbani AA (2015) Utilization of poly (acrylic acid)/cellulose graft copolymer for dye and heavy metal removal. *BioResources* 10(2):3112–3130
  148. Zhang G, Hui LY, Sun DP (2014) Dyes adsorption using a synthetic carboxymethyl cellulose-acrylic acid adsorbent. *J Environ Sci* 26(5):1203–1211. [https://doi.org/10.1016/S1001-0742\(13\)60513-6](https://doi.org/10.1016/S1001-0742(13)60513-6)
  149. Gupta VK, Pathania D, Agarwal S, Sharma S (2014) Amputation of congo red dye from waste water using microwave induced grafted *Luffa cylindrica* cellulosic fiber. *Carbohydr Polym* 111:556–566. <https://doi.org/10.1016/j.carbpol.2014.04.032>
  150. Sharma G, Naushad M, Pathania D, Mittal A, El-Desoky G (2015) Modification of *Hibiscus cannabinus* fiber by graft copolymerization: application for dye removal. *Desalin Water Treat* 54(11):3114–3121. <https://doi.org/10.1080/19443994.2014.904822>
  151. Goel NK, Kumar V, Misra N, Varshney L (2015) Cellulose based cationic adsorbent fabricated via radiation grafting process for treatment of dyes waste water. *Carbohydr Polym* 132:444–451. <https://doi.org/10.1016/j.carbpol.2015.06.054>
  152. Kumar V, Goel NK, Bhardwaj YK, Sabharwal S, Varshney L (2012) Development of functional adsorbent from textile cotton waste by radiation induced grafting process: equilibrium and kinetic studies of acid dye adsorption. *Sep Sci Technol* 47(13):1937–1947. <https://doi.org/10.1080/01496395.2012.664599>
  153. El-Mosallamy E-SH (2001) Improved dyeability and mechanical properties of wool fibers grafted with poly(acrylic acid) by gamma radiation. *J Macromol Sci A* 38(11):1167–1174. <https://doi.org/10.1081/MA-100107136>
  154. Cao W, Pei L, Zhang H, Wang J (2021) Sustainable wool fabric pad dyeing using reactive dyes in silicone non-aqueous medium. *Environ Chem Lett* 19(1):737–741. <https://doi.org/10.1007/s10311-020-01078-7>
  155. Gulrajani ML (1993) Dyeing of silk with reactive dyes. *Rev Prog Color Relat Top* 23(1):51–56. <https://doi.org/10.1111/j.1478-4408.1993.tb00096.x>
  156. Zhang G, Yi L, Deng H, Sun P (2014) Dyes adsorption using a synthetic carboxymethyl cellulose-acrylic acid adsorbent. *J Environ Sci* 26(5):1203–1211. [https://doi.org/10.1016/S1001-0742\(13\)60513-6](https://doi.org/10.1016/S1001-0742(13)60513-6)
  157. Hassan MS (2015) Removal of reactive dyes from textile wastewater by immobilized chitosan upon grafted Jute fibers with acrylic acid by gamma irradiation. *Radiat Phys Chem* 115:55–61. <https://doi.org/10.1016/j.radphyschem.2015.05.038>
  158. Suni S, Kosunen AL, Hautala M, Pasila A, Romantschuk M (2004) Use of a by-product of peat excavation, cotton grass fibre, as a sorbent for oil-spills. *Mar Pollut Bull* 49(11):916–921. <https://doi.org/10.1016/j.marpolbul.2004.06.015>
  159. Hubbe MA, Rojas OJ, Fingas M, Gupta BS (2013) Cellulosic substrates for removal of pollutants from aqueous systems: a review. 3. Spilled oil and emulsified organic liquids. *BioResources* 8(2):3038–3097
  160. Doshi B, Sillanpää M, Kalliola S (2018) A review of bio-based materials for oil spill treatment. *Water Res* 135:262–277. <https://doi.org/10.1016/j.watres.2018.02.034>
  161. Deschamps G, Caruel H, Borredon M-E, Bonnin C, Vignoles C (2003) Oil removal from water by selective sorption on hydrophobic cotton fibers. 1. Study of sorption properties and comparison with other cotton fiber-based sorbents. *Environ Sci Technol* 37(5):1013–1015. <https://doi.org/10.1021/es020061s>
  162. Onwuka JC, Agbaji EB, Ajibola VO, Okibe FG (2018) Treatment of crude oil-contaminated water with chemically modified natural fiber. *Appl Water Sci* 8(3):86. <https://doi.org/10.1007/s13201-018-0727-5>
  163. Cojocaru C, Macoveanu M, Cretescu I (2011) Peat-based sorbents for the removal of oil spills from water surface: application of artificial neural network modeling. *Colloids Surf A* 384(1):675–684. <https://doi.org/10.1016/j.colsurfa.2011.05.036>
  164. Wang J, Zheng Y, Wang A (2013) Coated kapok fiber for removal of spilled oil. *Mar Pollut Bull* 69(1–2):91–96. <https://doi.org/10.1016/j.marpolbul.2013.01.007>
  165. Gao Y, Zhou Y, Zhang X, Zhang L, Qu P (2012) Synthesis and characteristics of graft copolymers of poly (butyl acrylate) and cellulose with ultrasonic processing as a material for oil absorption. *BioResources* 7(1):0135–0147. <https://doi.org/10.15376/biores.7.1.135-147>
  166. Teli MD, Valia SP (2016) Grafting of butyl acrylate on to banana fibers for improved oil absorption. *J Nat Fibers* 13(4):470–476. <https://doi.org/10.1080/15440478.2015.1055034>
  167. Viju S, Brindha R, Thilagavathi G (2021) Surface modification of nettle fibers by grafting to improve oil sorption capacity. *J Ind Text* 50(8):1314–1329. <https://doi.org/10.1177/1528083719862879>
  168. El-Kelesh NA, Abd Elaal SE, Hashem A, Sokker HH (2007) Radiation-induced graft copolymerization of cellulosic fabric waste and its application in the removal of cyanide and dichromate from aqueous solution. *J Appl Polym Sci* 105(3):1336–1343. <https://doi.org/10.1002/app.26183>
  169. Takács E, Wojnárovits L, Koczog Horváth É, Fekete T, Borsa J (2012) Improvement of pesticide adsorption capacity of cellulose fibre by high-energy irradiation-initiated grafting of glycidyl methacrylate. *Radiat Phys Chem* 81(9):1389–1392. <https://doi.org/10.1016/j.radphyschem.2011.11.016>
  170. Desmet G, Takács E, Wojnárovits L, Borsa J (2011) Cellulose functionalization via high-energy irradiation-initiated grafting of glycidyl methacrylate and cyclodextrin immobilization. *Radiat Phys Chem* 80(12):1358–1362. <https://doi.org/10.1016/j.radphyschem.2011.07.009>
  171. Du J, Dong Z, Pi Y, Yang X, Zhao L (2019) Fabrication of cotton linter-based adsorbents by radiation grafting polymerization for humic acid removal from aqueous solution. *Polymers* 11(6):962. <https://doi.org/10.3390/polym11060962>
  172. Nasef MM, Nallappan M, Ujang Z (2014) Polymer-based chelating adsorbents for the selective removal of boron from water and wastewater: a review. *React Funct Polym* 85:54–68. <https://doi.org/10.1016/j.reactfunctpolym.2014.10.007>
  173. Nishihama S, Sumiyoshi Y, Ookubo T, Yoshizuka K (2013) Adsorption of boron using glucamine-based chelate adsorbents. *Desalination* 310:81–86. <https://doi.org/10.1016/j.desal.2012.06.021>
  174. Wongjaikham W, Wongsawaeng D, Hosemann P (2019) Synthesis of amidoxime polymer gel to extract uranium compound from seawater by UV radiation curing. *J Nucl Sci Technol* 56(6):541–552. <https://doi.org/10.1080/00223131.2019.1602485>
  175. Yin Z, Xiong J, Chen M, Hu S, Cheng H (2016) Recovery of uranium(VI) from aqueous solution by amidoxime functionalized wool fibers. *J Radioanal Nucl Chem* 307(2):1471–1479. <https://doi.org/10.1007/s10967-015-4534-2>
  176. Zhang F, Chen M, Hu S, Cheng H (2017) Chemical treatments on the cuticle layer enhancing the uranium(VI) uptake from aqueous solution by amidoximated wool fibers. *J Radioanal Nucl Chem* 314(3):1927–1937. <https://doi.org/10.1007/s10967-017-5548-8>
  177. Wen J, Li Q, Li H, Chen M, Hu S, Cheng H (2018) Nano-TiO<sub>2</sub> imparts amidoximated wool fibers with good antibacterial activity and adsorption capacity for uranium(VI) recovery. *Ind Eng Chem Res* 57(6):1826–1833. <https://doi.org/10.1021/acs.iecr.7b04380>

178. Wang Y, Zhang Y, Li Q, Li Y, Cao L, Li W (2020) Amidoximated cellulose fiber membrane for uranium extraction from simulated seawater. *Carbohydr Polym* 245:116627. <https://doi.org/10.1016/j.carbpol.2020.116627>
179. Othman SH, Sohah MA, Ghoneim MM, Sokkar HH, Badawy SM, El-Anadouli BE (2006) Adsorption of hazardous ions from radioactive waste on chelating cloth filter. *Radiat Phys Chem* 75(2):278–285. <https://doi.org/10.1016/j.radphyschem.2005.08.020>
180. Monier M, Akl MA, Ali WM (2014) Modification and characterization of cellulose cotton fibers for fast extraction of some precious metal ions. *Int J Biol Macromol* 66:125–134. <https://doi.org/10.1016/j.ijbiomac.2014.01.068>
181. Rahman ML, Sarjadi MS, Arshad SE, Yusoff MM, Sarkar SM, Musta B (2019) Kenaf cellulose-based poly(amidoxime) ligand for adsorption of rare earth ions. *Rare Met* 38(3):259–269. <https://doi.org/10.1007/s12598-018-1061-7>
182. Ng WJ (2006) *Industrial wastewater treatment*, vol 628.30950 N5. Imperial College Press, London
183. Hubbe MA, Metts JR, Hermosilla D, Blanco MA, Yerushalmi L, Haghighat F, Lindholm-Lehto P, Khodaparast Z, Kamali M, Elliott A (2016) Wastewater treatment and reclamation: a review of pulp and paper industry practices and opportunities. *BioResources* 11(3):7953–8091. <https://doi.org/10.15376/biores.11.3.Hubbe>
184. Robinson T, McMullan G, Marchant R, Nigam P (2001) Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. *Bioresour Technol* 77(3):247–255. [https://doi.org/10.1016/S0960-8524\(00\)00080-8](https://doi.org/10.1016/S0960-8524(00)00080-8)
185. Bhatnagar A, Minocha A (2006) Conventional and non-conventional adsorbents for removal of pollutants from water—a review. *Indian J Chem Technol* 13(3):203–217
186. Hubbe MA (2015) New horizons for use of cellulose-based materials to adsorb pollutants from aqueous solutions. *Lignocellulose* 2(2):386–411
187. Omar H, Rohani S (2015) Treatment of landfill waste, leachate and landfill gas: a review. *Front Chem Sci Eng* 9(1):15–32. <https://doi.org/10.1007/s11705-015-1501-y>
188. Fingas M (2013) *The basics of oil spill cleanup*, 3rd edn. CRC Press, Boca Raton. <https://doi.org/10.1201/9781420032598>
189. Gebald C, Wurzbacher JA, Tingaut P, Zimmermann T, Steinfeld A (2011) Amine-based nanofibrillated cellulose as adsorbent for CO<sub>2</sub> capture from air. *Environ Sci Technol* 45(20):9101–9108. <https://doi.org/10.1021/es202223p>
190. Zaini N, Kamarudin KS (2018) Effect of concentration on amine-modified kenaf as a sorbent for carbon dioxide adsorption in a pressure swing adsorption system. *ChemEngineering* 2(2):23–35. <https://doi.org/10.3390/chemengineering2020023>

**Publisher's Note** Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.