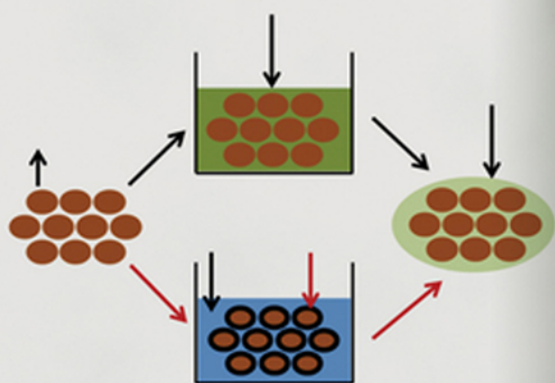
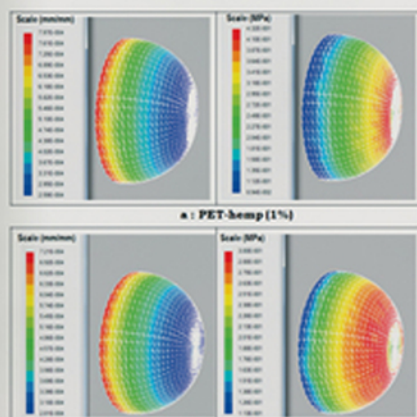


Handbook of Composites from Renewable Materials

FUNCTIONALIZATION



Edited by **VIJAY KUMAR THAKUR,**
MANJU KUMARI THAKUR and **MICHAEL R. KESSLER**

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**Volume 4
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Edited by

**Vijay Kumar Thakur, Manju Kumari Thakur
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To my parents and teachers who helped me become what I am today.
Vijay Kumar Thakur

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Preface

The concept of green chemistry and sustainable development policy impose on industry and technology to switch raw material base from the petroleum to renewable resources. Remarkable attention has been paid to the environmental-friendly, green, and sustainable materials for a number of applications during the past few years. Indeed, the rapidly diminishing global petroleum resources, along with awareness of global environmental problems, have promoted the way to switch toward renewable resources-based materials. In this regard, biobased renewable materials can form the basis for a variety of eco-efficient, sustainable products that can capture and compete markets presently dominated by products based solely on petroleum-based raw materials. The nature provides a wide range of the raw materials that can be converted into a polymeric matrix/adhesive/reinforcement applicable in composites formulation. Different kinds of polymers (renewable/nonrenewable) and polymer composite materials have been emerging rapidly as the prospective substitute to the ceramic or metal materials, due to their advantages over conventional materials. In brief, polymers are macromolecular groups collectively recognized as polymers due to the presence of repeating blocks of covalently linked atomic arrangement in the formation of these molecules. The repetitive atomic arrangements forming the macromolecules by forming covalent links are the building blocks or constituent monomers. As the covalent bond formation between monomer units is the essence of polymer formation, polymers are organic or carbon compounds of either biological or synthetic origin. The phenomenon or process of polymerization enables to create diverse forms of macromolecules with varied structural and functional properties and applications. On the other hand, composite materials, or composites, are one of the main improvements in material technology in recent years. In the materials science field, a composite is a multiphase material consisting of two or more physically distinct components, a matrix (or a continuous phase) and at least one dispersed (filler or reinforcement) phase. The dispersed phase, responsible for enhancing one or more properties of matrix, can be categorized according to particle dimensions that comprise platelet, ellipsoids, spheres, and fibers. These particles can be inorganic or organic origin and possess rigid or flexible properties. The most important resources for renewable raw materials originate from nature such as wood, starch, proteins, and oils from plants. Therefore, renewable raw materials lead to the benefit of processing in industries owing to the short period of replenishment cycle resulting in the continuous-flow production. Moreover, the production cost can be reduced by using natural raw materials instead of chemical raw materials. The waste and residues from agriculture and industry have also been used as alternative renewable resources for producing energy and raw materials such as chemicals, cellulose, carbon, and silica.

For polymer composites applications, an intensifying focus has been directed toward the use of renewable materials. Biobased polymers are one of the most attractive candidates in renewable raw materials for use as organic reinforcing fillers such as flex, hemp, pine needles, coir, jute, kenaf, sisal, rice husk, ramie, palm, and banana fibres, which exhibited excellent enhancement in mechanical and thermal properties. For green polymer composites composed of inorganic reinforcing fillers, renewable resources-based polymers have been used as matrix materials.

Significant research efforts all around the globe are continuing to explore and improve the properties of renewable polymers-based materials. Researchers are collectively focusing their efforts to use the inherent advantages of renewable polymers for miscellaneous applications. To ensure a sustainable future, the use of biobased materials containing a high content of derivatives from renewable biomass is the best solution.

This volume of the book series "*Handbook of Composites from Renewable Materials*" is solely focused on the "*Functionalization*" of renewable materials. Some of the important topics include but not limited to: Chitosan-based biosorbents: oil spill clean-up by textiles; pyridine and bipyridine end-functionalized polylactide; functional separation membranes from chitin and chitosan derivatives; acrylated epoxidized flaxseed oil bioresin and its biocomposites; encapsulation of inorganic renewable nanofiller; chitosan coating on textile fibers for functional properties; surface functionalization of cellulose whiskers for nonpolar composites; impact of chemical treatment and the manufacturing process on mechanical, thermal, and rheological properties of natural fibers-based composites; biopolymers modification; review on fibers from natural resources; strategies to improve the functionality of starch-based films; the effect of gamma radiation on biodegradability of natural fibers; surface functionalization through vapor-phase-assisted surface polymerization (VASP) on natural materials from agricultural by-products; okra bast fiber as potential reinforcement element of biocomposites; silane coupling agent used in natural fiber/plastic composites; composites of olefin polymer/natural fibers: the surface modifications on natural fibers; surface functionalization of biomaterials; thermal and mechanical behaviors of biorenewable fibres-based polymer composites; natural and artificial diversification of starch; and role of radiation and surface modification on biofiber for reinforced polymer composites.

Several critical issues and suggestions for future work are comprehensively discussed in this volume with the hope that the book will provide a deep insight into the state-of-the-art of "*Functionalization*" of the renewable materials. We would like to thank the Publisher and Martin Scrivener for the invaluable help in organization of the editing process. Finally, we would like to thank our parents for their continuous encouragement and support.

Vijay Kumar Thakur, Ph.D.
Washington State University – USA

Manju Kumari Thakur, M.Sc., M.Phil., Ph.D.
Himachal Pradesh University, Shimla, India

Michael R. Kessler, Ph.D., P.E.
Washington State University – USA

Chitosan-Based Biosorbents: Modifications and Application for Sequestration of PPCPs and Metals for Water Remediation

Dipali Rahangdale¹, G. Archana¹, Rita Dhodapkar^{2*} and Anupama Kumar^{1*}

¹Department of Chemistry, Visvesvaraya National Institute of Technology (V.N.I.T),
Nagpur, India

²Waste Water Technology Division, CSIR-National Environmental Engineering
Research Institute, Nagpur, India

Abstract

Contamination of aquatic media by organic and inorganic pollutants is a serious environmental problem that affects the reuse of water obtained from treated domestic or industrial waste water. This chapter discusses the occurrence, persistence, bioaccumulation, adverse risk assessments on ecosystem by the pollutants along with an overview of the limitations, drawbacks, and recent challenges of some advanced effective techniques like advance oxidation processes and ozonation for the remediation of pollutants. It also highlights new horizons for their removal using new and cost-effective treatment technologies. The chapter addresses novel adsorbents including chitosan-based derivatives that have been used for sequestration of pollutants for water purification. Specific recognition sites can be incorporated within the chitosan-based biosorbents using molecularly imprinted technique for enhancing its adsorption capacity. Computer-aided design of chitosan-based biosorbents provides assistance in choice of precursors and porogen and proves to be a rapid and economical option to optimize the imprinting conditions for achieving higher removal efficiency.

Keywords: PPCPs, chitin, chitosan, grafting, adsorption, heavy metals, cross-linker

1.1 Introduction

Over the past few decades, water pollution has led to serious health effects to the flora and fauna as well as the human beings due to continuous entry of emerging pollutants and is the major environmental concern these days. It is found to be a major cause for poor nutritional standards and development in children (water pollution, Wikipedia). Pollution is caused by a variety of human activities such as industrial, agricultural,

*Corresponding authors: anupamakumar@chm.vnit.ac.in, drkumaranupama21@gmail.com;
ritadhodapkar@hotmail.com

domestic as well as due to the release of untreated/treated sewage or industrial waste water to the surrounding water bodies (Ledezma *et al.*, 2012; shen *et al.*, 2011; Heberer *et al.*, 2002; Jiang *et al.*, 2013). Recent developments in analytical chemistry have led to better sensitivity and detection of compounds present in microgram or nanogram levels in water. Thus, a new group of pollutants have emerged and gained attention as these compounds end up into the aqueous environment as an upshot causing adverse effect on the living organisms as well as ecosystem. These contaminants mainly are endocrine disrupting compounds (EDCs), synthetic and naturally occurring hormones, pharmaceuticals and personal care products (PPCPs), herbicides, fungicides, pesticides, insecticides, bug repellents, etc. (Xu *et al.*, 2013; Shraim *et al.*, 2012; Kot-Wasik *et al.*, 2007; Arany *et al.*, 2013; Dodgen *et al.*, 2014; Ziyalan *et al.*, 2011; Pal *et al.*, 2013).

PPCPs are diverse galaxies of chemicals defined as, compounds used in daily life for personal hygiene and cosmetic purpose as well as in agribusiness that help to enhance the growth and improve the health of livestock. Pharmaceuticals include antidepressants, tranquilizers, psychiatric drugs, cancer drugs, pain killers, anti-inflammatory, antihypertensive, antiseptics, lipid regulators (e.g., cholesterol medication), oral contraceptives, synthetic hormones, drugs for enhancing sexual performance, antibiotics, and many other classes and types of drugs. Personal care products are chemical compounds used for personal hygiene and for beautification. Personal care products include variety of compounds, such as perfumes, musk, shampoos, deodorants, hair dye, oral hygiene product, hair spray, cosmetic, nail polish, sun screen, body lotion, lipstick, etc. (Huber *et al.*, 2003; Belgiorino *et al.*, 2007; Molinos-Senante *et al.*, 2014; Sun *et al.*, 2014; Neamțu *et al.*, 2014; Gavrilescu *et al.*, 2015; Kosjek *et al.*, 2012).

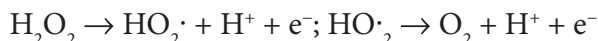
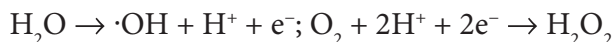
PPCPs are consistently entering into various aqueous sources by the discharge of treated and untreated sewage and go undetected due to no standards levied on the municipal bodies by the regulatory agencies. Persistence of PPCPs in water bodies also finds their way into the ground water and finally into drinking water. Providence and fate of PPCPs in aquatic environment is a serious matter of public concern, and recently more scrutiny has been paid to these emerging pollutants in water bodies (Ellis *et al.*, 2006; Bolong *et al.*, 2009; Gunnarsdottir *et al.*, 2013). Several investigations reveals the presence of PPCPs in trace concentrations level ranging from ngL^{-1} to $\mu\text{g L}^{-1}$ in various environmental matrix, possibly due to inefficacious removal by sewage treatment plants (Esplugas *et al.*, 2007).

Many of these PPCPs are ubiquitous, persistence, and suffer biotransformation leading to the production of highly pernicious metabolites. The first alarming negative impact of the levels of PPCPs was communicated by Stumm-Zollinger in 1965 and Tabak and Bunch in 1970. Some of the negative effects caused by PPCPs include toxicity to aquatic organisms by disruption of endocrine system or genotoxicity, development of pathogenic resistant bacteria, and feminization in male fish. The recent reports on PPCPs and endocrine disruptors (EDCs) cannot be ignored due to high levels reported and at the same time these surface water bodies are source of drinking water (Sanderson *et al.*, 2004; Escher *et al.*, 2011; Mostofa *et al.*, 2013; Blair *et al.*, 2013; Bu *et al.*, 2013; Tsui *et al.*, 2014; Zhang *et al.*, 2014; Kostich *et al.*, 2014). Therefore, it is essential to remove these emerging contaminants to make the environment healthy for the survival.

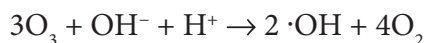
The conventional treatment processes includes primary, secondary, and tertiary treatment stages, which are ineffective for the removal of PPCPs and their metabolites (Huerta-Fontela *et al.*, 2011). Keeping the limits and draw backs of the conventional techniques, advance treatment methods like advanced oxidation processes (AOPs) have been continuously researched to resolve these problems. AOP can be considered as an effectual water operational process for remediation of most PPCPs. AOP can be defined as the oxidation process which generate very powerful hydroxyl radicals, with high oxidation potential. They are nonselective and are utilized to degrade various non biodegradable organics and inorganics. The concept of AOP was established by Glaze and coworkers in 1987. These includes homogeneous process using energy such as UV, electrical energy, ultrasound, and without energy such as H_2O_2 in the presence of catalyst or H_2O_2 in presence of ozone and heterogeneous process such as catalytic ozonation, photo catalysis, ozonation, heterogeneous catalysis, etc. Although ozonation and oxidation are considered to be effective technique, it has limitation such as high cost, likely production of toxic metabolites as well as the removal efficiency depends on the ozone dose or oxidant dose added, which limits their applicability in sewage treatment process (Kim *et al.*, 2007; Sarkar *et al.*, 2014; Mboula *et al.*, 2015).

The schematic reaction for generation of OH radical in the presence of various oxidants is given below:

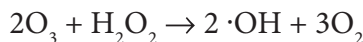
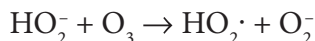
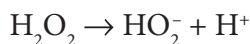
- H_2O_2 mechanism:



- Ozonation at elevated pH:



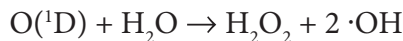
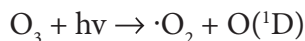
- Ozonation in the presence of H_2O_2 :



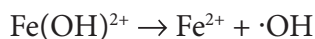
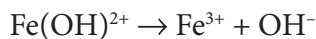
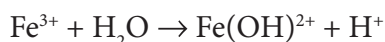
- Fenton system ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$):



- Ozone–UV radiation:



- Photo-Fenton and Fenton-like systems:



Keeping these drawbacks and limitations and in view of the application of more comprehensive sewage treatment protocols as well as with the implementation of improved advance technologies, development of specific process with increased removal efficiency is required. Investigation of the effectiveness of cost-effective techniques for removal of PPCPs as an option for polishing of treated wastewater needs to be investigated.

Increase in industrial activities and uprising human population has led to increase in the heavy metals concentration in our surrounding environment which are considered toxic, as they cannot be degraded. These pollutants can enter into various water resources including surface and ground water bodies either from consumer and industrial waste or natural processes such as heavy rain which help to release the trapped heavy metals from soils. These micropollutants has ability to penetrate into the tissues and cells of various living organisms like plant, animals, and human beings and can disrupt the functional activity of vital internal components (Liu *et al.*, 2013). Though the toxic effect of metals was perceived since ancient times, toxicological studies of these pollutants were revealed in earlier 1868. Therefore, it is a quite important to remove these toxic pollutants from aqueous system to safeguard the health and growth of living organisms (Ngha *et al.*, 2011; Chen *et al.*, 2009).

Among various techniques, adsorption is considered to be efficient for removal of these pollutants from water bodies. A variety of materials such as commercial granular activated carbon, bituminous coal, products from agro waste, and their carbonization products have been used as adsorbents. However, the economical status of the developing countries limits the use of costly advanced activation techniques (Fan *et al* 2011; Ramesh *et al.*, 2008). Hence, other environment-friendly natural biopolymers such as lignin, cellulose, chitosan, and carbohydrates have been widely used for synthesis of biosorbents with high adsorption capacities. They exhibit several “green” properties such as biodegradability, easy accessibility, low cost, reusability, highly abundance, high mechanical strength, and stability and can be effectively used for environmental, biomedical applications, water remediation, as well as cosmetic, paint, pesticide, and many more products (Thakur *et al.*, 2015; Thakur *et al.*, 2008; Thakur *et al.*, 2014; Singha *et al.*, 2008; Singha *et al.*, 2012; Thakur *et al.*, 2011).

Chitosan is a one of the low-priced adsorbents which is derived from chitin as an N-deacetylated product which is the second most copious natural biopolymer. Chitin is a nitrogenous polysaccharide present in internal and exoskeletal structure of invertebrates. The waste generated due to this natural polymer is one of the serious pollution issues in coastal surface areas. In countries like India, US, Australia, Japan, Poland, and Norway, these biopolymers are now commercially available. Research is ongoing in the world to maximize the use of chitin/chitosan with functional modifications to make it useful for various applications. These natural resources are waiting for a market.

These biodegradable polymers with good physical, chemical, and mechanical properties have also gained attention in the area of adsorption. Combined with the advantage of abundant availability and low price, their use has been prevalent in the pollution control operations (Verma *et al.*, 2004; Ngha *et al.*, 2011). The structure of chitosan is represented in Figure 1.1 which depicts the presence of residual 2-acetamido-2-deoxy-d-glucopyranose units and (1→4) linked 2-amino-2-deoxy-d-glucopyranose units.

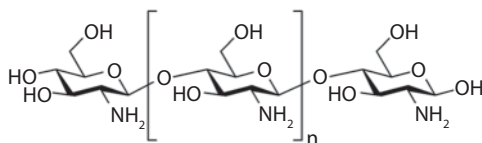


Figure 1.1 Structure of chitosan.

The presence of multiple functional groups like primary amino, acetamido, and hydroxyl groups on chitosan is responsible for its high chemical reactivity and therefore supports its use for removal of PPCPs and metal ions. Chitosan exhibits flexible chain-like structure. The reactive amino group has the ability to bind the transition metal ions selectively keeping the alkali and alkaline metal ions free. In acidic solutions, chitosan protonates and exhibits cationic behavior, thus making it suitable for the removal of anions through ion exchange (Wang & Chen, 2014). Glucosamine and acetylglucosamine units of chitosan make it heterogeneous in nature.

The principal parameters that significantly influence the physicochemical properties of chitosan are degree of deacetylation (i.e., number of free amino groups), weight, and crystallinity. Studies reveal that degree of deacetylation is mostly less than 95% for a commercial chitosan. Degree of deacetylation can be attained with additional deacetylation steps which results in partial depolymerization, and therefore became increasingly costly with implementation of revolutionary and propitious processes. Therefore, highly deacetylated chitosan is commonly used only for biomedical applications (Mourya & Inamdar, 2008; Thakur & Thakur, 2014).

Acetamide groups on chitin are less reactive as compared to the amino groups on chitosan. Deacetylation of chitin is therefore helpful for generation of the free amino groups of the chitosan that interact with the target analytes. The free electron doublet on amino group are mainly responsible for the adsorption of target analyte, thus making the presence of the amino groups as a key parameter in sorption techniques. The usability of these heterogeneous biopolymers mainly depends on the extent of its solubility in acidic medium. Chitosan with degree of deacetylation greater than 60% has the advantage of being soluble in acidic and insoluble in aqueous and organic medium. Its crystalline structure is due to the extensive intramolecular hydrogen bonding in chains and intermolecular hydrogen bonding in sheets. Various methods such as infrared spectroscopy and NMR analysis are generally used to evaluate the degree of deacetylation (Guibal, 2004).

1.2 Modification of Chitosan

Modification of chitosan is essential to enhance its adsorption capacity and specificity because of its low selectivity and poor recycling. A modification by chemical or physical processes can improve its mechanical and chemical properties (Mourya & Inamdar, 2008).

1.2.1 Physical Modification

Chitosan cannot be used as such for adsorption because of its low stability and reactivity. However, its versatility allows it to be easily modified into different forms such

Table 1.1 Physically modified chitosan derivative.

Sr. no.	Metal ion	Chitosan derivative	Reference
1	Sr(II)	Magnetic chitosan	Chen <i>et al.</i> , 2012
2	Cd(II)	Chitosan activated carbon composite	Hyadri <i>et al.</i> , 2012
3	Pb(II) Ni(II)	Chitosan magnetite composite	Tran <i>et al.</i> , 2010
4	Cr(VI)	Zero valent iron chitosan composite	Liu <i>et al.</i> , 2012
5	Cr(VI)	Zero valent iron chitosan composite	Liu <i>et al.</i> , 2010
6	Cu(II), Zn(II), Pb(II)	Cross-linked chitosan	Chen <i>et al.</i> , 2008
7	Au(III), Pt(IV), Pd(IV)	Glycine modified cross-linked CTS resin	Ramesh <i>et al.</i> , 2008

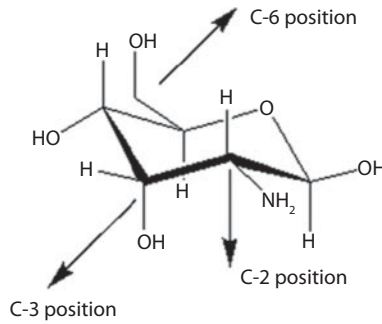


Figure 1.2 Chitosan.

as nanomaterials, beads, hydrogel, resin, membrane, fiber, etc. with increased adsorption efficiency. The increase in adsorption efficiency of physically modified chitosan is mainly due to increase in porosity and surface area. Physically modified chitosan can be used for various applications such as environmental, biomedical, cosmetics, and textile industries; thus, a great attention has been given by researchers to enhance the properties of chitosan by this method (Miretzky & Cirelli, 2009). A cross-linking agent during the process of casting is required to synthesize chitosan in the form of beads, which may decrease the adsorption efficiency of chitosan (Chen *et al.*, 2009; Miretzky & Cirelli, 2009). The use of physically modified chitosan for the metal ion adsorption is summarized in Table 1.1.

1.2.2 Chemical Modification

Chemical modification of chitosan helps to improve its stability and solubility properties during application. This can be done either through a cross-linking reaction or through grafting of a reactive agent containing functional group onto amino at C-2 position and/or hydroxyl group present at C-3 and C-6 position in chitosan (Figure 1.2). Amino groups

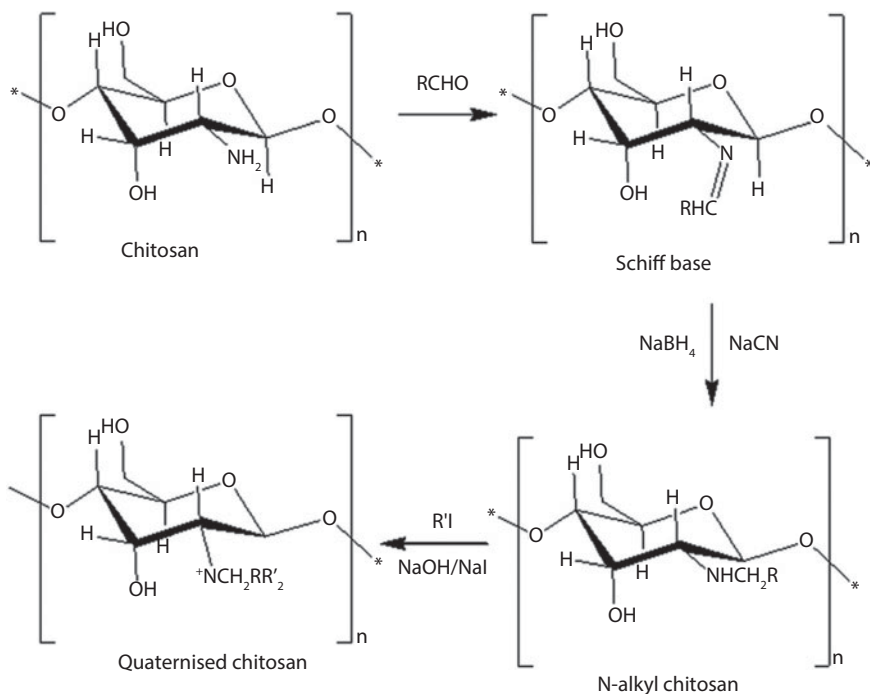


Figure 1.3 Quaternisation of amino group of chitosan.

on chitosan molecule undergoes two types of reaction: (i) quaternization of amino group and (ii) reaction with aldehydic functional group as can be seen in Figure 1.3.

1.2.2.1 Cross-Linking

Cross-linking with a bi-functional reagents such as ethylene glycol diglycidyl ether (EGDE) (Ramesh *et al.*, 2008; Liu *et al.*, 2010), glutaraldehyde (GLA) (Lu *et al.*, 2013), and mono-functional reagent such as epichlorohydrin (EPI) are the most common methods of cross-linking. Bifunctional cross-linking agent such as GLA and EGDE cross-links with chitosan through an amino group (Figure 1.4), thus reducing the number of active sites for any target pollutant. Monofunctional cross-linking agent such as EPI reacts with both amino and hydroxyl groups (as shown in Figure 1.5) which not only retains the spatial structure of the adsorbents but also results in availability of more amino groups for the target pollutant adsorption via noncovalent interaction. Thus EPI is a better cross-linking agent for chitosan. EPI may react only with amino groups of chitosan by opening of its ether group, during grafting of an amino group through Schiff's base reaction. On the other hand, the chloride group of EPI is capable of interacting with other functional groups or amino groups on chitosan as can be seen in Figure 1.6 (Chen *et al.*, 2008, 2009).

GLA cross-linked electron spun chitosan nanofiber mats was synthesized by Li and his coworkers for the efficient removal of Pb (II) ion using Electrospinning technique. The binding efficiency of chitosan nanofiber mats was greater than simple chitosan-based

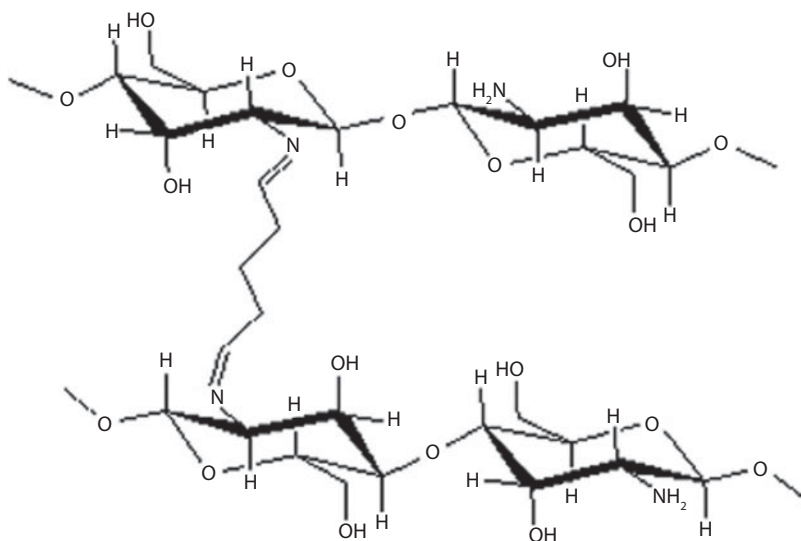


Figure 1.4 Glutaraldehyde cross-linked chitosan.

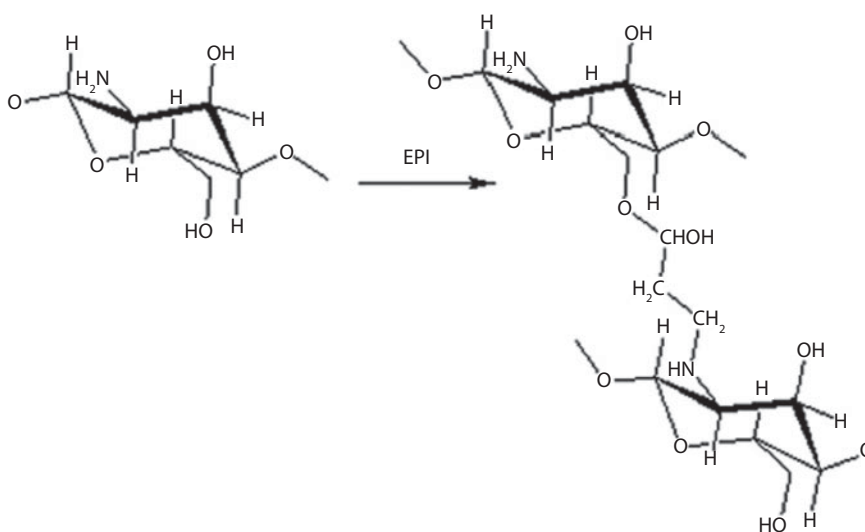


Figure 1.5 Chitosan cross-linked with epichlorohydrin.

adsorbents, which might be due to the increase in surface area and porosity of chitosan nanofiber mats (Li *et al.*, 2013).

The composites of chitosan/*Sargassum* sp. were synthesized by Huijuan Liu *et al.* for the selective removal of copper ion using EPI as a cross-linking agent. Ion-imprinting technique was used for the synthesis of adsorbent. The greater efficiency of chitosan-based adsorbents for copper ion removal was mainly due to the large number of active groups such as amine, hydroxyl, and acetamido present on chitosan molecule (Liu *et al.*, 2010).

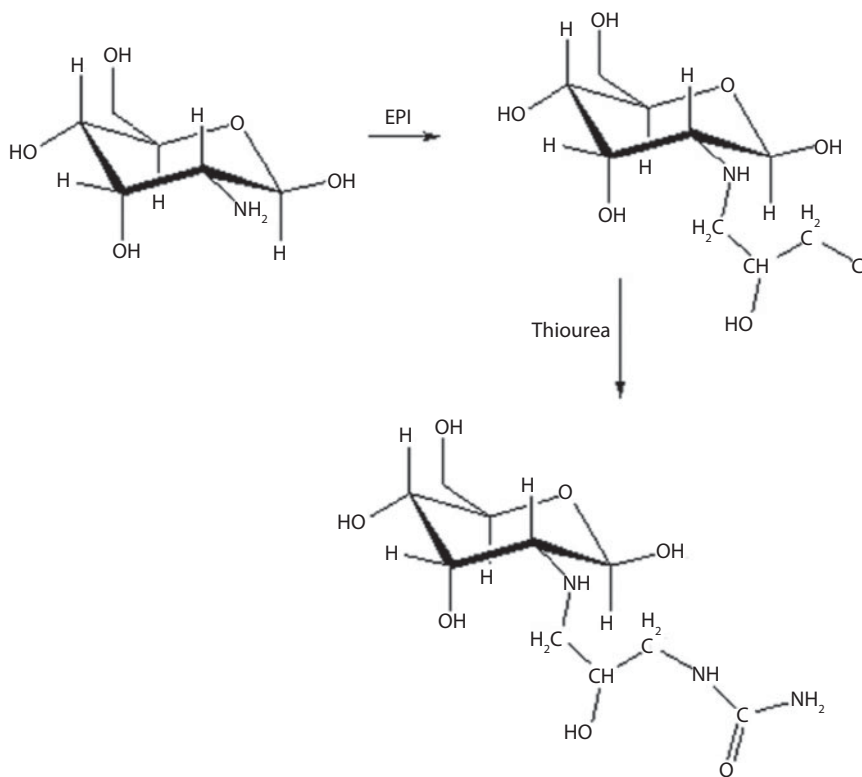


Figure 1.6 Functionalisation of chitosan using epichlorohydrin as cross-linking agent (Thiourea grafted chitosan).

Magnetic chitosan-based microspheres were synthesized by Fan *et al.* using thiourea-grafted chitosan as a monomer, EPI as a cross-linker for the effective removal of Ag^+ ion. The high binding efficiency of modified chitosan-based adsorbent was due to the chelation of Ag^+ ion with the electron doublet present on the amino group of chitosan and sulfur atom of thiourea (Fan *et al.*, 2011). The chitosan-based resin was synthesized by Limin Zhou *et al.*, using GLA as a cross-linking agent for the removal of U (IV) ion (Zhou *et al.*, 2012).

The disadvantage of cross-linking of chitosan is decrease in its adsorption capacity due to the participation of active groups such as amino and hydroxyl groups present on its backbone in cross-linking reaction which in turn affects the uptake of target analyte. Therefore, derivatization of chitosan with a particular reagent containing greater number of active binding site can be an excellent alternative to increase its performance during adsorption (Mourya & Inamdar, 2008).

1.2.2.2 Grafting

Amongst the various techniques available for enhancing the adsorption capacity of chitosan, graft copolymerization is found to be the most efficient technique for its chemical modification. Numbers of derivatives of chitosan have been synthesised by reacting

it with appropriate reagent with the aim of increasing the active site for specific binding of the targeted analyte. The concentration of monomer, initiator used, time, temperature, solvent, etc. are the parameters that need to be controlled for proper grafting. The properties of derivatized chitosan depend on the chemical nature of grafted functional group onto chitosan (Mourya & Inamdar, 2008; Liu *et al.*, 2013; Thakur *et al.*, 2011; Singha *et al.*, 2008).

1.2.2.2.1 Computational Study

Molecular modeling studies can prove to be very useful for the selection of suitable grafting agent for the functionalisation of chitosan (Farrington *et al.*, 2006). Molecular modeling studies include several steps, as given below (Pardeshi *et al.*, 2012).

In the first step, the 3D structures of the molecules are drawn using Chem draw and Chem 3D Ultra Software and minimized to the most stable conformation of molecule. Finally, input file is generated using atomic coordinates of the stable conformer.

The second step is the optimization of geometry that attempts to find the configuration of minimum energy of the molecule. The procedure calculates the wave function and geometry initially and then proceeds to search new geometry of a lower energy. This is repeated until the lowest energy geometry is found. B3LYP 6-31G basic set is generally used for the optimization of geometry of molecule.

In the last step, i.e., frequency calculation the favorability of the reaction is determined by calculating Gibbs free energy change during the reaction using the formula given below:

$$\Delta G = G_{\text{functionalized CTS}} - [G_{\text{CTS}} + G_{\text{grafting agent}}] \quad (1.1)$$

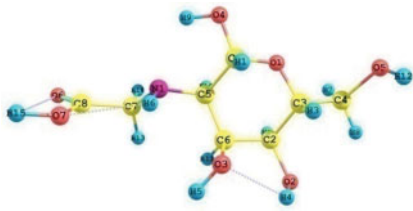
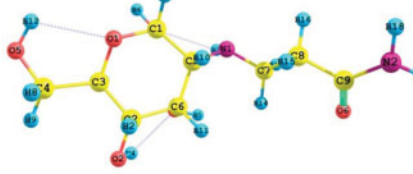
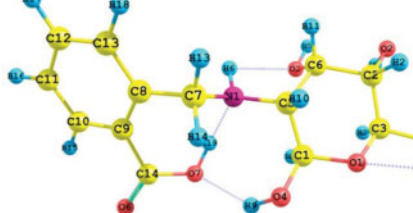
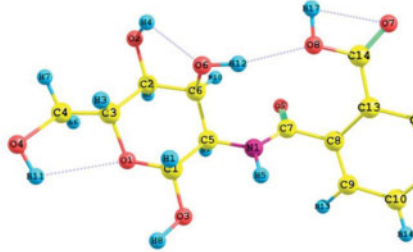
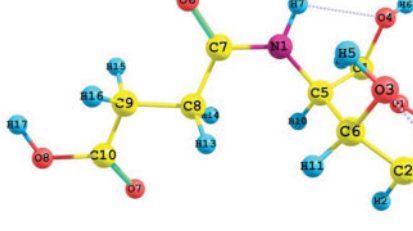
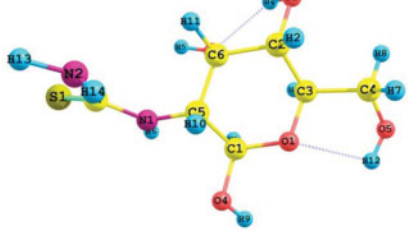
where ΔG is the change in Gibbs free energy of functionalized chitosan, $G_{\text{functionalized CTS}}$ is the Gibbs free energy of functionalized Chitosan, G_{CTS} is the Gibbs free energy of chitosan and $G_{\text{grafting agent}}$ is the Gibbs free energy of grafting agent. Table 1.2 gives the ΔG values for the grafted chitosan using different grafting agents. For example, acrylamide-grafted CTS with $\Delta G = -17.98$ Kcal/mol is found to be the most stable derivative.

Novel thiourea-grafted chitosan-based chelating agents onto chitosan backbone through grafting reaction using GLA as a cross-linking agent (Fan *et al.*, 2011) and dithiocarbamate-modified chitosan by reacting with carbon disulfide have been reported (Liu *et al.*, 2013).

Bingjie and coworkers used ion-imprinting technique for the selective removal of Pb (II) ions. They synthesized the Pb (II) ion-imprinted chitosan-based polymer beads using dithiocarbamate-grafted chitosan as a functional monomer and EPI as a cross-linking agent for removal of Pb (II) ions. Dithiocarbamate derivative of chitosan was used in order to increase its selectivity and removal efficiency for Pb (II) ion as dithiocarbamate derivative is found to act as a good chelating agent for Pb (II) ion (Liu *et al.*, 2013).

Derivatization of cross-linked chitosan polymer enhances its efficiency with respect to its specificity, binding capacity and time needed for the removal of target analyte. Recently, molecular imprinting method has been widely employed for improving the binding capacity of derivatized cross-linked chitosan polymer by incorporating specific recognition sites for the target analyte (Chen *et al.*, 2009; Li *et al.*, 2013).

Table 1.2 Gibbs free energy for the various derivatives of chitosan.

Derivative of CTS	Structure	ΔG (Kcal/mol)
Carboxy methyl CTS		460.78
Acrylamide grafted CTS		-17.98
Carboxy benzyl CTS		75.21
Pthalic acid derivative of CTS		-13.27
Succinyl Derivative of CTS		-6.88
Thiourea grafted CTS		-17.98

1.2.3 Molecular Imprinting Technique

Synthesis of the molecularly imprinted polymers (MIP) using chitosan as functional monomer for enhancing the adsorption efficiency of chitosan-based adsorbents has been lately reported. MIP has selective recognition sites for the template molecule which are generated within the polymer by allowing the template molecule to react with the functional monomer in the presence of cross-linking agent and porogen solvent, to form a template monomer complex. The type of interaction involved, may be either covalent or noncovalent, which results in the formation of highly cross-linked stable polymeric matrix. Finally, the template molecule is extracted using the suitable solvent which is able to disrupt the interaction between template and monomer, thus resulting in the vacant binding sites with the shape and size complementary to the structure of template molecule. Ion-imprinting technique is one of the branches of MIP which is found to be very efficient for the removal of toxic heavy metal ions. The schematic presentation for the synthesis of molecularly imprinted chitosan-based polymer is shown in Figure 1.7. Metal ion-imprinted chitosan shows wide range of application which includes the removal of PPCP's and other pollutants (Chen *et al.*, 2009; Fan *et al.*, 2011; Zhou *et al.*, 2012; Liu *et al.*, 2011).

In the ion-imprinting process, the recognition of metal ion depends on the size of metal ion, its valency and coordination number. The ion-imprinted cross-linked chitosan-based polymers, show high stability in an acidic media. MIPs are characterized by high physical and chemical stability under high temperature, pressure, acidic

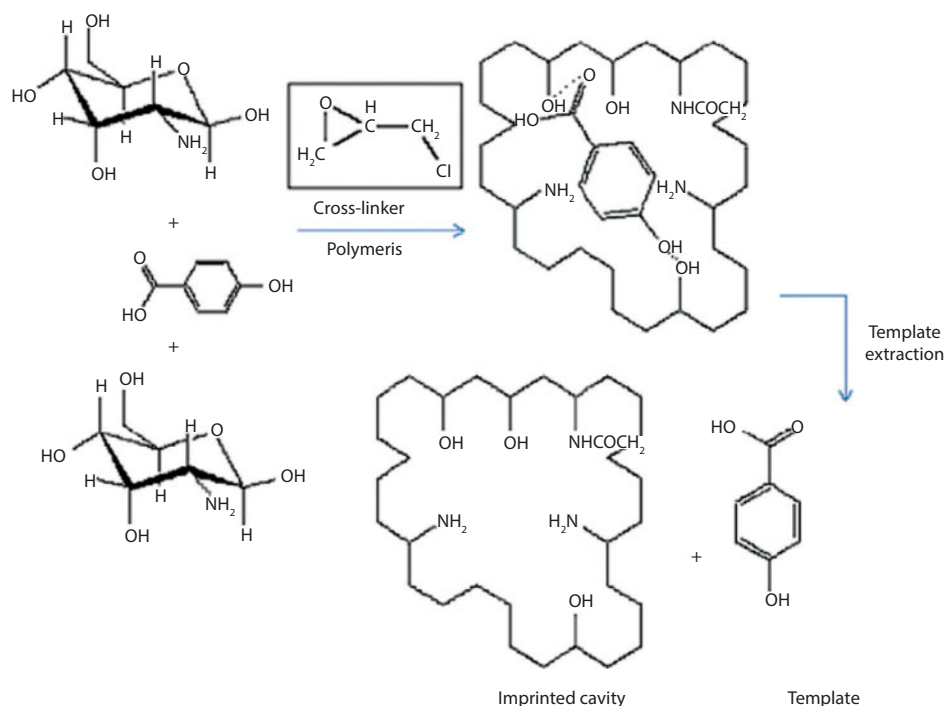


Figure 1.7 Schematic representation for the synthesis of molecularly imprinted chitosan based adsorbents.

and basic media because of their cross-linked structure and therefore can be reused for several cycles without any remarkable loss in adsorption capacity (Guibal, 2004; Varma *et al.*, 2004).

Recently, chitosan-based molecularly imprinted polymers have been receiving much attention in order to develop a simple and convenient method, for simultaneous removal of inorganic and organic pollutant, keeping in view, the new technological developments involving eco-friendly materials (Weng *et al.*, 2013; Li *et al.*, 2008). In such polymers, organic molecule can be used as template molecule in presence of a functional monomer (chitosan itself is a functional monomer) to form a template – monomer complex and further the process of polymerization is performed in the presence of a suitable cross-linking agent. Thereafter, the template molecule is extracted using a suitable solvent, thus leading to the formation of polymeric matrix with permanent memory for template molecule (organic pollutant). The polymer now can selectively rebind the template (organic pollutant) from waste water. Chitosan contain active sites in large numbers and all the sites does not participate in the cross-linking reaction. Some of the active sites may therefore participate in metal ion uptake (Zhang *et al.*, 2013; Wang *et al.*, 2014; Fan *et al.*, 2012).

Chitosan-based ion imprinted polymers have been reported to be used for metal ions removal, and some of these examples are listed in Table 1.3. The use of chitosan-based molecularly imprinted polymers for removal of organic pollutants like PPCPs is listed in Table 1.4. Metal ion-complexed chitosan have been found to be effective for the removal of organic pollutants such as PPCPs and is reported in Table 1.5. The literature reveals that the work reported on the simultaneous removal of organic and inorganic pollutants using chitosan based adsorbents is scarce as can be seen in Figure 1.8.

Molecularly imprinted polymer has gained much attention in environmental application due to its high binding/adsorption efficiency and selectivity towards target

Table 1.3 Chemically modified ions imprinted chitosan derivatives.

Sr. no.	Metal ion	Chitosan derivative	Year	Reference
1	Pb(II)	CTS Nanofibre Mat	2013	Li <i>et al.</i> , 2013
2	Pb(II)	Dithiocarbamate modified CTS	2013	Liu <i>et al.</i> , 2013
3	Cu(II)	CTS/saragassum sp. Composite	2011	Liu <i>et al.</i> , 2011
4	As(II)	α -Fe ₂ O ₃ impregnated CTS	2011	Liu <i>et al.</i> , 2011
5	UO ₂ ⁺	CTS/PVA cross-linked hydrogel	2010	Liu <i>et al.</i> , 2010
6	Ag(I)	Magnetic thiourea CTS	2011	Fan <i>et al.</i> , 2011
7	U(VI)	Magnetic CTS resin	2012	Zhou <i>et al.</i> , 2012
8	Cu(II)	Carboxymethyl chitosan	2006	Sun <i>et al.</i> , 2006
9	Co(II)	Ion imprinted chitosan	2012	Nishad <i>et al.</i> , 2012
10	Ag(I)	CTS/TEA Composite	2012	Zhang <i>et al.</i> , 2012
11	Cu(II), Zn(II), NI(II), Pb(II)	Cross-linked chitosan	2009	Chen <i>et al.</i> , 2009

Table 1.4 Chitosan based MIP for adsorption of organic compounds.

Sr. no.	Chitosan composite	Organic compound	Year	Reference
1	Chitosan Fe ₃ O ₄ composite	Carbamazepine	2013	Zhang <i>et al.</i> , 2013
2	Chitosan MIP	Methandrostenlone	2012	Wang <i>et al.</i> , 2014
3	Magnetic chitosan composite	Alizarin red	2012	Fan <i>et al.</i> , 2012
4	Chitosan/graphene oxide composite	Sulphame-thoxazole	2013	Huamin <i>et al.</i> , 2013
5	Chitosan/ γ -Fe ₂ O ₃ /fly-ash cenosphere	Bisphenol A and 2,4,6 trichlorophenol	2011	Pan <i>et al.</i> , 2011

Table 1.5 Molecularly imprinted Chitosan based adsorbents for simultaneous removal of organic and inorganic compounds.

Sr. no.	Chitosan composite	Inorganic compound	Organic compound	Reference
1	Chitosan stabilised bimetallic Fe-Ni composite	Cd(II)	Amoxicillin	Weng <i>et al.</i> , 2013
2	Chitosan TiO ₂ composite	Ni(II)	Methyl orange	Li <i>et al.</i> , 2008
3	Chitosan TiO ₂ composite	Cd(II)	2,4-dichloro phenol	Chen <i>et al.</i> , 2012

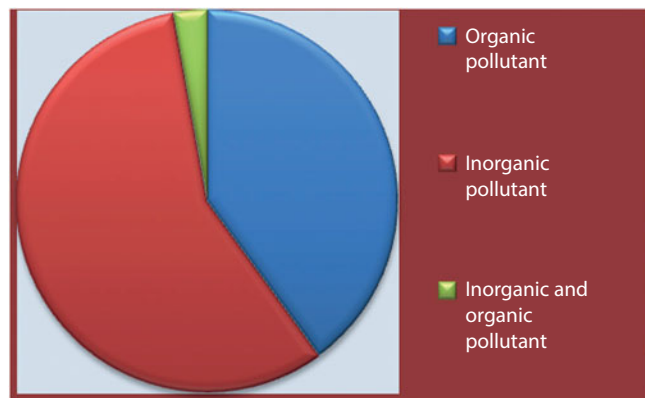


Figure 1.8 Reported literature (from 2010–2014) on work done on adsorption of 1) inorganic 2) organic 3) inorganic and organic compound onto molecularly imprinted chitosan composites.

analyte; however, research to increase its efficiency is in progress. Some researchers have attempted to use some reagents as cross-linker in the coagulation bath during the synthesis of MIP to prevent the involvement of active groups in cross-linking reaction to some extent (Zhang *et al.*, 2012).

Novel Ag(I) ion-imprinted chitosan composites in the form of hydrogel and gel beads were prepared by Liang Zhang and coworkers using ion-imprinting technique for the selective removal of Ag ion. In the synthesis of the chitosan beads, triethanolamine (TEA) solution was used as a coagulation bath to enhance its efficiency. When the binding capacity of beads in the form of hydrogel and gel was compared, it was observed that hydrogel form of beads had higher binding capacity for Ag ion than gel beads, which may be due to the increase in porosity and surface area in case of hydrogel beads. However, in the case of gel beads, low adsorption capacity was attributed to the decrease in the porosity and increase in the compactness as the chitosan content. The reason for the decrease in the porosity of the gel beads was reported due to the coordinate bonding between the metal Ag (I) and chitosan/TEA. Thus we can say that the adsorption capacity of beads depends on their surface area and porosity (Zhang *et al.*, 2012).

Liu and coworkers successfully synthesized an innovative chitosan biopolymer impregnated with $\alpha\text{-Fe}_2\text{O}_3$ for arsenic metal decontamination from aqueous matrix using ion-imprinting technique (Liu *et al.*, 2011).

Recently, great attention has been given to endow the physiochemical properties of chitosan-based polymer. Liu and coworkers synthesized a composite chitosan/PVA (polyvinyl alcohol) cross-linked hydrogel for the decontamination of uranyl ion. Uranyl ion-imprinted hydrogel was synthesized by using EGDE as cross-linking agent. Hydroxyl group present on chitosan molecule takes part in cross-linking reaction making amine group free for uranyl ion uptake (Liu *et al.*, 2010).

Zhou and coworkers synthesized magnetic chitosan resin to overcome the problem of separation of chitosan-based adsorbent from aqueous solution during application. U (VI)-ion-imprinted magnetic chitosan resin was synthesized by using U (VI) as template and GLA as a cross linking agent for decontamination of U (VI) ion from aqueous solution (Zhou *et al.*, 2012).

1.3 Interactions of Chitosan-Based MIP Sorbents with Pollutants (Organic & Inorganic)

1.3.1 Organic Molecule

Chitosan-based molecularly imprinted polymers have chitosan as functional monomers which interacts with the template during polymerization in following ways (Vasapollo *et al.*, 2011; Yan *et al.*, 2006).

1.3.1.1 Covalent

In this approach, the type of bonding involved between the template and monomer during the synthesis of chitosan-based molecularly imprinted polymers and its application

is covalent. Generally, covalent approach is not applied for synthesis of chitosan-based MIPs as they are characterised by slow uptake rate during its application and subsequent extraction of the template.

1.3.1.2 *Noncovalent*

In the noncovalent approach, the interaction during the process of synthesis and its application is noncovalent between the template and the monomer.

1.3.1.3 *Semicovalent Interaction*

In this case, the bonding between the target analyte and monomer during the process of synthesis is covalent while during its application non covalent interactions dominate.

1.3.2 **Inorganic Molecule (Metal Ions)**

Chitosan exhibits tendency to interact with metal ions through different mechanism depending on the pH of solution, nature of metal ion and matrix containing metal ions. The uptake of metal ion is mainly through the amine groups and to some extent, though hydroxyl groups present on chitosan. At neutral pH, the amine groups of CTS donate its lone pair of electron to metal cation and thus remove the metal cation through chelation mechanism. However, in the acidic pH, the amine groups of chitosan are protonated and responsible for the removal of metal anion through electrostatic force of attraction between protonated amine groups and metal anions (Ramesh *et al.*, 2008; Jiang *et al.*, 2013).

1.3.2.1 *Chelation (Coordinate Covalent Bond)*

Hard and soft acids and bases (HSAB) theory introduced by Ralph Pearson explains the stability of metal complexes and the mechanisms of their reactions. According to the Pearson theory, Lewis acid and bases are further classified as hard and soft Lewis acid and bases. Hard acids and bases are small and nonpolarizable, whereas soft acids and bases are larger and more polarizable. According to HSAB theory, hard acids prefer binding to the hard bases to give ionic complexes, whereas the soft acids prefer binding to soft bases to give covalent complexes. The type of interaction involved during complex formation is coordinate interaction. Coordinate interaction is found to be stronger than electrostatic force of attraction. Electrostatic interaction between metal ions depends on the valency and size of metal ion whereas coordinate interaction depends on softness parameter of Lewis acid and bases. Chitosan shows greater tendency to react with transition metal ions due to the availability of vacant d and f orbitals in these metals compared to the non transition metal ions. However, some of the derivatives of chitosan like phosphorylated chitosan exhibits tendency to interact with non transition metal ions also (Ramesh *et al.*, 2008; Zhou *et al.*, 2009).

1.3.2.2 *Ion Exchange/Electrostatic Attraction*

The metal ion removal efficiency by chitosan is governed by the degree of deacetylation of chitosan i.e. the number of available free amine groups. At neutral or

slightly acidic pH, almost half the population of total amine groups get protonated and are involved in the uptake of metal anions through electrostatic force of attraction, while the free amine groups are responsible for the uptake of metal cations by donating their lone pair of electrons through chelation mechanism. The efficiency of adsorption by chitosan increases at highly acidic pH (Ramesh *et al.*, 2008; Zhou *et al.*, 2009).

1.4 Applications of Chitosan

1.4.1 Applications of Metal-Loaded Chitosan

There are several applications of metal-loaded chitosan such as

- i. sorption of organic and Inorganic pollutants
- ii. catalytic applications which include oxidation, reduction, and degradation of organic compounds

1.4.1.1 Sorption of Organic and Inorganic Pollutants

It has been reported that the metal-complexed chitosan-based adsorbents are more efficient in the removal of organic compounds. For example, Shinde and coworkers synthesized Cu(II)-, Fe(III)-, La(III)-, Mo(VI)-, and Zr(IV)-loaded chitosan adsorbents for the removal of arsenic ion. Amongst all these metal ion-loaded chitosan adsorbents, iron-loaded chitosan was found to be most efficient for arsenic removal followed by La(III)-loaded chitosan adsorbent (Shinde *et al.*, 2013).

A novel nanocomposite $\text{Fe}_3\text{O}_4/\text{ZrO}_2/\text{chitosan}$ was synthesized by Hualin Jiang *et al.*, and used for the simultaneous removal of nitrate and phosphate at acidic pH through electrostatic force of attraction between the adsorbents and pollutants. At acidic pH, the binding efficiency of nanocomposites was high, mainly due to easy protonation of the $-\text{NH}_2$ group of chitosan and $-\text{OH}$ group of ZrO_2 which are responsible for the uptake of nitrate and phosphate (Jiang *et al.*, 2013).

Bingjie Liu *et al.* synthesized Zr (IV) ion-loaded chitosan beads using dithiocarbamate-grafted chitosan as a functional monomer, for the fluoride ion removal. The chitosan molecule was grafted with dithiocarbamate group to increase its specificity and binding efficiency for target analyte. When the binding capacity of Zr (IV)-loaded dithiocarbamate-modified chitosan bead was compared with simple chitosan bead, it was observed that dithiocarbamate-modified chitosan beads had much more binding efficiency for fluoride ion than the chitosan beads. This clearly indicated that the amino and hydroxyl groups present on chitosan were not responsible for fluoride ion uptake (Liu *et al.*, 2013).

Chitosan gel beads immobilized with Cu^{2+} ion have been used for the selective adsorption of histidine from a mixed solution containing histidine and tryptophan. The hydroxyl and amine groups present on chitosan molecule were mainly responsible for the separation of histidine amino acid from a mixture through chelation mechanism. The high binding efficiency of chitosan beads for histidine molecule was mainly due to the high porosity and surface area of chitosan gel beads. Chitosan gel beads

immobilized with Cu^{2+} can also be used for the separation of IgG molecule using chromatography technique (Bai *et al.*, 2008).

1.4.1.2 Catalytic Applications

Earlier, commercially available adsorbents such as alumina and activated carbon were used as a support for the metals for the catalytic application. However, recently, great deal of attention has been paid to the use of metal-complexed MIPs for supporting catalytic metals. Selectivity of chitosan-based molecularly imprinted material and the versatility of metal–ligand coordination offer an attractive tool for the design and synthesis of novel catalytic system and are found to be more successful than conventional supports (Guibal, 2004).

Xiluang Weng prepared chitosan-stabilized bimetallic Fe/Ni nanoparticles for the concurrent removal of amoxicillin and Cd (II) from aqueous solution, using the liquid phase reduction method. Bimetallic nanoparticles were found to be more efficient for individual removal of amoxicillin and Cd (II) as compared to the simultaneous removal of amoxicillin and Cd (II). Nanoscale zero valent iron because of its properties like stability and dispersibility can also be effectively used for the metal ion removal. However, during its application for metal ion removal, it was observed that it gets oxidized easily resulting in the loss of its reactivity, which can be overcome by bimetallic Fe/Ni nanoparticles (Weng *et al.*, 2013).

Tingyi and coworkers successfully synthesized the iron-loaded chitosan beads for the decontamination of chromium from wastewater by adsorption of chromium onto the surface of chitosan beads and its further reduction (Liu *et al.*, 2012).

1.4.2 Other Applications of Chitosan

Compared to other adsorbents, chitosan finds application in the medical field mainly due to its resistance towards the fluids (bile juice, pancreatic juice, and urine) in the human body. Chitosan can be used as adsorbable sutures and wound dressing materials in form chitosan fibres which can accelerate up to 75% in healing wounds as reported in the literature (Dutta *et al.*, 2004). In spite of poor solubility chitosan can be used in vast array by modifying its original structure physically or chemically, depending on its area of applications. It can be used in various fields ranging from cosmetic applications to plant protection and polishing wastewater. Due to its anti fungicidal nature and compatibility with lots of biologically active components it can be used in cosmetics, oral care, skin and hair care. Polycationic nature of chitosan makes its application in water engineering as a flocculating, chelating agents as well as heavy metal trapper. It can also be used for the removal of color from dye house effluents, removal of metal ions and petroleum products from wastewater and recycling of food processing waste, etc. Chitosan is used in the paper industry due to its biodegradable nature for the production of toilet papers, wrapping papers, cardboard and packing food materials, etc. Furthermore, it is used in textile industry, food processing, agriculture, chromatographic separations, and preparation of solid batteries in the form of gel in dyes, in LED and NLO products and its components. Along with the industrial application, it can also be used in biomedical area in designing artificial membranes

similar to kidney systems mainly because of its tensile strength and permeability. Chitosan is useful in tissue engineering, as a material for the replacement of parts of the knee, hip, vascular replacement, etc. Chitosan is also useful in wound dressing, burn treatment, designing artificial skin, ophthalmology as well as drug delivery systems (Dutta *et al.*, 2004).

1.5 Conclusion

Chitosan-based biosorbents are efficient, naturally abundant, biodegradable polymer for the removal of pollutants like metals and PPCPs. The presence of the functional groups like hydroxyl and amino groups on chitosan helps in its easy derivatization. Chitosan can be easily modified into different physical form due to its versatility. As chitosan shows distinct physical, chemical, and biological properties, it finds use in different fields like cosmetic, pharmaceutical industries, water remediation, paper industry, textile industry, drug delivery system, etc. Percent deacetylation and molecular mass governs the properties of chitosan which needs to be selected as per the application. Chitosan can be a better alternative to other polysaccharides; however, grafting a suitable active functional group on its surface needs to be thoroughly researched to enhance its properties for better applications. Chitosan-based materials have shown outstanding sorption for organic (PPCPs) and inorganic pollutants and abundant literature is available on the sequestration of either organic or inorganic pollutant from aqueous media. However, work reported on the simultaneous removal of PPCPs and metals from water is scarce. Thus, it is necessary to develop novel chitosan-based adsorbents for simultaneous removal of organic and inorganic pollutants.

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Oil Spill Cleanup by Textiles

D.P. Chattopadhyay^{1*} and Varinder Kaur²

¹*Department of Textile Chemistry, Faculty of Technology & Engineering,
The Maharaja Sayajirao University of Baroda, Vadodara, India*

²*Department of Chemistry, Guru Nanak Dev University, Amritsar, India*

Abstract

Oil is an important source of power. Oceans and inland transportation are the best mode of transportation from the production sites to demanding areas for its consumption. Mishandling of containers or accident causes slippage of oil on roads, rivers, and ocean. This chapter critically reviews the most capable approaches to fabricate different textile fibers including natural and synthetic for the purpose of oil recovery from spilled zone. Recovery of oil from the used fibers assembly and its reuse are two very important aspects critically discussed in this chapter. Furthermore, the physical property of oil and the absorbent materials significantly influences the oil sorption and retention performance of the absorbents. The theory of oil sorption, techniques for oil spill cleanup, main features of oil sorbent fibers, and test methods for evaluation of these properties are also elaborated here.

Keywords: Oil spill, textile fibres, sorption, cleanup, recovery and retention

2.1 Introduction

Crude oil is one of the most important natural resources of the energy. This raw form of oil can also be used to produce heat, run machines means of transportations. It is usually used as vital material to make many chemical and synthetic products (Annunciado *et al.*, 2005). Oil spillage is a common problem caused due to mishandling of containers or it may also be caused accidentally on roads, rivers, and ocean. As these severe domino effects disturb the aquatic life and plants; therefore, oil spill cleaning is a vital start goal for all environmental concerns (Wardley-Smith, 1983), and there is a need for advanced sorbent materials having an efficient sorption capacity for this target. Relative importance of textile fibers is now being considered as elective applicant for oil absorbents (Wardley-Smith, 1983).

*Corresponding author: dpchat6@gmail.com

2.2 Causes of Oil Spilling

During the production, transportation from one place to another place, storage for further processing and refining according to its end uses of crude oil, oil spillage may occur and become the cause of environmental toxic waste after spilling.

In many industries like petroleum, manufacturing units, refineries and rayon industries, the risk of oil spill is high through derivation process, transmission or burning up of these complexes, when it has been used as energy source (Annunciado *et al.*, 2005). Another source of oil pollutant is oil reservoirs which can generate and store a huge quantity of spilled oil in water (Yang *et al.*, 2000). As seawater consists of large amount of salt, when crude oil gets spilled in sea water it makes an oil-in-water emulsion which is a combination of water hydrocarbons, fresh water and sea water in addition to salt (National Academy of Science, 1985).

2.3 Problems Faced Due to Oil Spilling

Floating film in the form of oil-in-water emulsion is usually formed when oil comes in contact with water, and it is mandatory to get rid of this film before it is discarded into the surroundings. In conservative manure methods, those microorganisms which are responsible for biodegradation may be affected or toxicated by a small quantity of spilled oil (Fei *et al.*, 2009). The odor and taste of spilled oil are undesirable due to the formation of toxic components. There are very much chances of entering these components along with their toxicity into human food chains and affects our health along with marine life and vegetations (Hussein *et al.*, 2009; Sayed *et al.*, 2006).

When crude oil discharged to the marine surroundings through accidental spillage or leakage in water, it endures a ample range of climate processes, which comprise evaporation, dissolution, dispersion, photochemical oxidation, microbial degradation, adsorption onto suspended materials, agglomeration, etc. (Jordan *et al.*, 1980). All these physicochemical modifications motivate oil dissolution in seawater (Payne *et al.*, 1985).

The volatile elements evaporate rapidly (Figure 2.1). Several average-sized polycyclic aromatic hydrocarbons are having very little solubility. On the other side, those

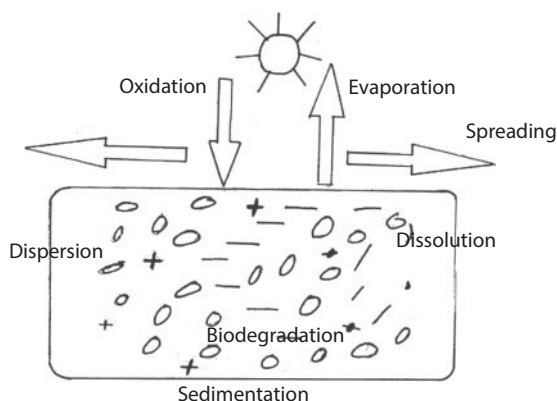


Figure 2.1 Physico-chemical changes during 'Weathering' process of oil from the sea surface.

products, which are degraded by sun light and natural microbes, are extremely soluble. The climate conditions usually perform rapidly in initial period of weathering process (Beom-Goo *et al.*, 1999; Lee *et al.*, 1999).

2.4 Oil Sorption Phenomenon

In sorption, two words frequently used are absorption and adsorption. Sorption is an efficient way to clean up water which can take place by two mechanisms. Absorbents permit oil to enter into voids of the material they are fabricated, while, adsorbents draw oil to their surfaces but do not permit it to go through into the sorbents (Karan *et al.*, 2011). Adsorption is an efficient and commercial method to decrease the ecological difficulties of spilled oil and cleaning of these kinds oil contamination.

Sorbents can be referred as insoluble substances which can recover liquids during above said absorption and adsorption. The efficiency of oil sorption in the sorbents is highly affected by following factors (Teas *et al.*, 2011):

1. Oleophilicity and hydrophobicity of sorbents (Adebajo *et al.*, 2003)
2. Recovery of oil from sorbents
3. Quantity of oil absorbed per unit mass of sorbent
4. Reusability of sorbents
5. Biodegradability of sorbent

2.4.1 Absorption and Adsorption

Absorbents hold fluids via their molecular arrangement by swelling of the sorbents (Adebajo *et al.*, 2003). An occurrence illustrated by the manner and the extent of transfer of liquid into an absorbing material is called absorbency, and this particular phenomenon is usually occurred only to those structures where there is affinity between the fluid and the absorbent. The capillary force is the major dynamic strength for the transport of the mass of the liquid into a material and this driving force can be increased by an additional force like gravity or pressure (Mitul, 2004).

Substantial adherence or bonding or binding of individual ions, atoms and molecules of an adsorbate onto the shell of another molecule of adsorbent is known as adsorption.

Adsorbents attract the spilled oil toward the surface of the sorbent (Adebajo *et al.*, 2003). Adsorption of particles forms different coatings which results in one layer over the earlier adsorbed layers due to physical adsorption. When the contacting molecules of adsorbate and adsorbent are held together by van der Waals' force, then physical adsorption occurs. The adsorption in which an exchange of electron takes place between adsorbate and surface of the adsorbent is known as chemical adsorption.

There are three rate determining steps in adsorption (Figure 2.2):

1. The adsorbate disperses from the main body of watercourse to the external surface of the adsorbent particle.
2. The adsorbent particles migrate from comparatively minute part of the external surface near the pores in all adsorbate. There are plenty

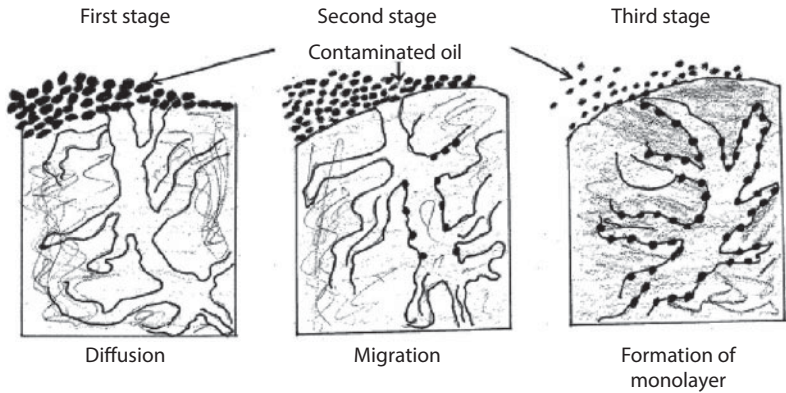


Figure 2.2 Schematic mechanism of the adsorbate disperses from the main body of waterway.

Table 2.1 Methods for oil spill cleanup (Zahed *et al.*, 2005; Zhu *et al.*, 2001).

Category	Example technology
Natural method	Natural attenuation
Physical method	Booming and skimming Wiping with absorbent materials Mechanical removal Low-pressure flushing Washing Cutting vegetation Stripping
Chemical methods	Dispersants Demulsifiers Gelling agents (solidifiers) Surface film chemicals <i>In situ</i> burning
Biological methods	Bioremediation Phytoremediation

accessible pores present on the surface of the adsorbate that is why the bulk of adsorption generally takes place in these pores.

3. The pollutant molecule sticks to the surface in the pore.

2.5 Removal of Oil Spill

The kind of skill which is used in the cleanup process of an oil spill depends on the type, feature, and amount of spilled oil (Zhu *et al.*, 2001).

In recent times, various inflexible international laws are in force in order to control the contamination of sea water by spilled oil. There are various methods for cleaning of spilled oil like physical, chemical, and biological methods. These methods are listed in Table 2.1 (Zhu *et al.*, 2001; Zahed *et al.*, 2005).

In physical method, the removal of oil is generally carried out by using dispersants, oil booms, sorbents, and skimmers (Wardley-Smith, 1983). On the other side, in the chemical method, it is carried out by different techniques like solidifiers, *in-situ* burning and dispersions (Azzam *et al.*, 2008). Due to insufficient trace level adsorption and high cost, these methods are less in use. Removal of oil by sorption technique is usually considered to be one of the most efficient techniques used for complete removal of spilled oil (Ceylan *et al.*, 2009). As cheap and highly efficient methods are the need of scientists, the use of sorbent materials is a good option for combating oil spill in marine life and vegetation (Choi *et al.*, 1996). The number of environmentally adapted thermal and biological methods is available for disposal of oil and its sludge. Operating cost and initial high capital requirement are the main drawbacks of thermal methods. Composting, treatments in slurry bioreactors and aerated lagoons belong to biological methods.

2.5.1 Sorbents for Removing Spilled Oil

The materials used to soak up the liquids are called sorbents. The efficiency of sorbent depends on its hydrophilic and oleophilic natures, in addition to these the other important features consist of retention of oil in excess of time, recovery of oil from sorbents, amount of oil sorbed per unit weight of sorbent, and reusability or biodegradability of sorbent (Melvold *et al.*, 1988; Halligan *et al.*, 1976; The International Tanker Owner Pollution Federation Limited, 1980; Schatzberg, 1971).

Oil-absorbing stuff is commonly considered as a useful material for cleaning up and recovering the spilled oil. These materials can be categorized into three different classes (Adebajo *et al.*, 2003; Deschamps *et al.*, 2003; Schatzberg, 1971):

1. Inorganic mineral materials
2. Organic natural (vegetable) materials
3. Synthetic organic materials (Adebajo *et al.*, 2013; She *et al.*, 2010)

The inorganic mineral materials comprised of fly ash, perlite, zeolites, vermiculite, silica, organic clay, and graphite (Teas *et al.*, 2001; Banerjee *et al.*, 2006). Oil sorption capacity of these materials is in general low (Schatzberg, 1971). Synthetic organic polymers like polypropylene, polyethylene, and polyacrylate are promising oil-absorbing substances in this (Teas *et al.*, 2001). Synthetic materials like polypropylene and polyurethane froth are the most commonality recommended sorbents in oil spill cleanup as these sorbents are extremely oleophilic and hydrophobic in nature (The International Tanker Owner Pollution Federation Limited, 1980; Schatzberg *et al.*, 1972).

A drawback of these substances is that their degradation rate is slow when it is compared with the mineral or vegetable materials. Organic natural materials engross a lot of agricultural goods, like cotton fiber, sawdust, kapok fiber, kenaf, milkweed corn cob, wood fiber, and straw (Annuciado *et al.*, 2005; Deschamps *et al.*, 2003b; Choi, 1996; Choi and Cloud, 1992; Choi and Moreau, 1993). Some studies resulted that organic vegetable products showed inferior buoyancy properties, comparatively low oil sorption behavior, and also squat hydrophobicity (Schatzberg, 1971). Canada Environmental Protection Services, studied oil sorption capacity per unit weight of sorbent which has been determined for various sorbents.

Table 2.2 Oil sorption capacities of some typical sorbents (Ross, 1991).

Sorbent	Diesel	(g oil/g sorbent)	Crude-1 day	(g oil/g sorbent)
Alfob	2.51	2.88	3.71	5.84
CCD wood chips	0.54	0.78	1.84	3.65
Clay	–	0.76	1.21	1.59
Cork	4.65	3.78	3.82	2.14
Oclansorb	9.07	6.16	6.76	5.51
Sawdust	4.08	5.29	6.65	9.75
Wool	9.54	14.07	19.80	11.70
Alsorb II	14.56	16.15	18.90	22.15
Eco oil sorbent	13.23	16.98	23.15	12.64
E100	11.04	9.99	16.01	14.73
Foam “X”	5.32	7.48	10.77	14.17
Graboil	18.62	10.17	8.19	6.71
Hazorb	9.52	8.49	7.03	4.36
Malasorb	7.98	9.16	11.91	10.34
Pig slimmer	8.14	4.94	5.93	5.57
S100	8.98	9.9	12.76	9.12

Ross, S. L., 1991. Selection Criteria and Laboratory Evaluations of Oil Spill Sorbents, Environmental Canada Protection Services EPS Manufacture Standard.

To clean up the spilled oil, many natural organic sorbents have been studied, e.g., raw sugarcane bagasse (Hussein *et al.*, 2008; Brandão *et al.*, 2010; Said *et al.*, 2009), carbonized peat bagasse (Hussein *et al.*, 2009), acetylated sugarcane bagasse (Chung *et al.*, 2011; Sun *et al.*, 2003), unprocessed and fatty acid-grafted sawdust for spilled oil and some other contaminants (Banerjee *et al.*, 2006; Shukla *et al.*, 2002), rice husk ash (Vlaev *et al.*, 2011), barley straw (Hussein *et al.*, 2009), banana trunk fiber bundles (Sathasivam and Haris, 2010), hydrophobic aerogels for spilled oil (Wang *et al.*, 2010; Site, 2001), and peat-based sorbents (Cojocar *et al.*, 2011).

A lot of superior-quality oil recuperating resources are presently available in the textile world as shown in Table 2.2. However, these materials are obsessed with a number of restrictions like they are expensive, having the limitation of their repeatedly use and having its own oil-saturated wastes which require very expensive post-treatment. All these things add on tremendous cost to the oil recovery process.

2.5.2 Textile Fibers for Removal of Oil Spills

Cellulose is one of the most important constituents of natural fibers that are being used in a number of applications (Thakur *et al.*, 2014a–c; Thakur & Thakur, 2014). Cellulose-rich sorbents like cotton, kapok, milkweed, and organic fibers have been pre-meditated for their prospective use in removing spilled oil as they are biodegradable in comparison to inorganic substrates, *viz.* graphite, wool, polypropylene, coal, and

chitosan. Milkweed and kapok possesses almost similar behavior for cleaning of oil like polypropylene fibers (Hubbe, 2013). Nevertheless, very less work has been reported on the oil sorption capacity of these two substrates. In case, if these organic materials prove high oil sorption capacity, in that case they may be used as the replacement of non-biodegradable synthetic sorbents in oil spill cleanup. Another important feature of materials used to absorb spill oil is biodegradability. Polypropylene is the most commonly used material to clean up oil, although it is not biodegradable and not floating, which is not helpful when oil floats on water (Das *et al.*, 2011). Furthermore, polypropylene has excellent absorption ability other than little retention ability. In addition to absorption of oil it is also very important that the absorbed oil should be retained and not released back into the surrounding (Fotheringham *et al.*, 2003).

Woven fibers contain diverse properties than loose fibers as nonwoven fibers are evaluated on the range of individual fibers (Pappu *et al.*, 2015). Innumerable pores in nonwoven fabrics help in absorption, transportation, and retention of oil. While using loose materials to absorb oil, increased surface area increases oil intake but on the other side, closely packed fibers decreases sorption because less pores are exposed to the oil. Lack of moisture may also influence the absorption of spilled oil. The configuration of pores can alter when dehydrated, causing some pores to close completely. Lesser density of fibers boosts oil sorption. If the spilled oil gets once absorbed, the lumens of natural fibers retain the absorbed oil. It is a problem with synthetic fibers that they cannot retain the oil (Hubbe, 2013).

2.5.2.1 *Kapok*

Due to high sorption capacity, biodegradability, essential hydrophobic nature, and low cost, kapok has good popularity as oil absorbent when it is compared with other natural materials (Annuciado *et al.*, 2005). It is a fiber derived from the fruits of silk-cotton tree. It is composed of cellulose (64%), lignin (12%), and polysaccharide (24%) (Karan *et al.*, 2011). A little quantity of waxy covering which covers the fiber surface makes it much hydrophobic or so-called water repellent (Choi *et al.*, 1993). Kapok fiber has established as an oil-absorptive material due to its hollow structure and hydrophobic properties. Kobayashi *et al.* (1977) studied this hollow cellulosic kapok fiber and according to their observations, the oil sorption of kapok fiber utilized in a rug, slab, band, or screen was around 1.5–2.0 times greater than that of polypropylene.

2.5.2.2 *Raw Bagasse*

A derivative of cane sugar processing is known as sugarcane bagasse which is generally produced in large amount in Iran and other countries. Previously, it has been employed either as a fuel for the boilers by sugar industry or as a raw material for the built-up of pulp and paper items, a variety of building panels and certain chemicals (Rowell *et al.*, 1991).

Behnood *et al.* (2014) studied raw bagasse for the adsorption of crude oil from salty waste water. According to the retort surface methodology (RSM) five parameters or factors, *viz.* temperature, salinity of water, pH, adsorbent dose, and initial oil content were measured. This experiment of optimization showed that the maximum crude oil removal is equal to 67.38% under the optimal condition of temperature of 46.53 °C,

salinity of 37.2 g/L, pH of 3, adsorbent dose of 9 g/L and initial oil content of 300×10^{-6} . This study shows that the bagasse appears to be an appropriate sorbent for adsorbing unfinished oil from sea water because of its low cost and could be used efficiently to recover oil spilled in bodies of refining or deep industrial dissipate water. Furthermore, this saturated bagasse can be burnt in incinerators, ovens, or condensation generators of large-scale industries. The hydrophobic biomass or raw bagasse produces a capillary power toward the adsorption of oils along with its high porosity because its tissues contain large surface area and big pores and have a tendency to adsorb unrefined contaminants through substantial and chemical mechanisms similar to charcoal (Gurgel *et al.*, 2008).

2.5.2.3 Cotton

Both oil and water can be effectively absorbed by cotton fibers. Being a rich source of cellulose, it considers as a biodegradable material (Anthony, 1994). It possesses low density and available in abundant form which make it an economical sorbent. Due to high oil absorbency coefficient, it can absorb oil 80 times more of its own weight.

As the oil sorption ability of natural fibers depends mostly on the surface voids and the surface composition of fibers, the sorption of oil decreases with the increase in the fibrous sorbent density. It is found that the oil sorption of cotton fiber is controlled by adsorption on the fiber surface and capillary action through its lumen (Choi *et al.*, 1993). The number of mechanisms has been studied on oil sorption by raw cotton (Onuma Carmody, 2007; Choi *et al.*, 1993). This sorption can be occurred either by one or in various combinations of different mechanisms which have been listed below:

- A. As raw cotton fibers are having irregular surface morphology; therefore, adsorption by physical trapping on the fiber face occurs during sorption phenomenon.
- B. Since there is a deposition of waxes inside the cuticle of the cotton fibers, adsorption by interactions between waxes on fiber surface and oils is there which occurs owing to their hydrophobic contact and van der Waals' forces due to their likeness as hydrocarbons (White, 2010).
- C. Capillary action from end to end the cuticles to the fiber lumen via diffusion of oil (Choi *et al.*, 1993).
- D. Capillary action via its empty lumen from fibers ends.

Johnson *et al.* (1973) showed the prospective for the utilization of cotton fiber in oil spill cleanup. Additional thorough information is required, yet prior to any subsequent application of cotton fiber can be ready in oil spill cleanup.

2.5.2.4 Milkweed Fibers

Milkweed floss (*Asclepias*), which is nurtured or naturally grown in a few states in the United States, is a hollow cellulosic material (Knudsen, 1990). Milkweed floss, especially, is expected to have high oil sorption capacity because of its high wax content and its hollow structure similar to kapok. The use of milkweed fibers for oil spill cleaning is one of the good quality choices. Its fibers have been reported to have empty structure so

as to provide huge interspatial region to entrap and retain oil (Kopayashi *et al.*, Japanese Patent 138). The existence of large quantity of wax on fiber surface is responsible for oil sorption by milkweed floss. When it is compared with cotton fibers, milkweed fibers have larger and noncollapsing lumen through which the maximum oil absorption can be occurred due to their more void volume. It is reported that at room temperature, 1 g of its fibers can absorb 40 g of light crude oil. The diameter of its fiber is greater than its wall thickness. Chol *et al.* (1992) examined a hollow milkweed fiber and according to their results, the wall thickness of milkweed fibers is nearly 10% of the total diameter of the fiber. Jean Yves *et al.* (1993) reported that the range in diameter of the milkweed fibers is from 20 to 50 μm and the mean diameter & mean wall thickness of milkweed fiber are 22.4 and 1.27 μm correspondingly.

Furthermore, it was reviewed by Sherif (2013) that the milkweed fibers have high contents of ash, lignin and low contents of total extractives and hollocelluloses. This composition shows an absence of fibrous excellence when these fibers are compared with other natural fibers like cotton and kapok and it is due to high content of ash. This high content of ash is a severe problem because it hinders the chemical revival procedure, while it is used as a predecessor for cellulosic chemical industries (Sherif, 2013).

2.5.2.5 Human Hair

There are miscellaneous uses of human hair because of its unique properties such as exclusive chemical composition, sluggish degradation speed, lofty tensile strength, thermal insulation, elastic recovery, scaly surface, and sole interactions with water and oils. Its areas of applications also depend on the assortment of hair accessible, differing in conditions of five parameters like length, color, straightness or curliness, hair damage, and contamination.

Hair has good adsorbing ability for oils. Being a nonbiodegradable substance, a large quantity of human hair is cue day after day and discards into landfills as a waste product having no straight benefits. After observing its physical and chemical nature, experts looked at the opportunity of ruling a use for waste hair could be used to clean up oil spills and this adsorbed oil could be recovered or renewed in fuel pellets. This technique is one of the elaborate techniques to clean polluted areas in diverse environments after oil spills. Human hair can be used to facilitate cleanse the affected region, soak up the oil after that utilized as a successful energy source rather than discarding it. Jadhav *et al.* (2011) studied the ability of the human hair to adsorb a range of possible hazardous oils like motor oils, crude oils, and bilge oils and all of them have the risk of being spilled in earthly or aquatic atmospheres. They studied different hair colors and concluded that on the whole black hair showed the most excellent results for adsorbing the heavy crude oil as well as refined crude oil products such as jet fuel, lubricant oils, gasoline, and heating oils. They also used hair pellets as fuel to reduce global warming which has also been avert to offer the cleanest smolder of any solid fuel.

There is a very fascinated property of human hair surface which is very useful in oil–water separation and this property is that it has a high affinity for oils which is much higher than its affinity for water (Murthy *et al.*, 2004). After getting this property, a revolutionary effort was carried out by Phillip A. McCrory from Alabama, USA (McCrory *et al.*, 1995; Rodgers, 1998) and the use of booms and mats of human hair have been

increased to clean up coastal oil spills in the Philippines and the United States (MSNBC, 2006; Gustafson, 2010). In Oil–Water Separation and Oil Spill Remediation method, oil can be recovered by squeezing out the hair, which after that can be used again up to 100 times and this is the advantage which has not been found in other oil spill remediation methods. Together with this technique, up to 98% of the spilled oil can be recuperated. After that, these oily hair can be utilized to breed oyster mushrooms (Gustafson, 2010), which rot the oil or lubricant. Leftover hair can further be composted. Other methods are very expensive to clean crude oil in comparison of the process performed by using human hair to separate emulsified oil in water (Murthy *et al.*, 2004).

2.5.2.6 Polypropylene

Oil sorbent products manufactured by polypropylene fiber have been established as frequently used goods to clean up oil spill. Non biodegradability of polypropylene causes a number of environmental problems (Thakur *et al.*, 2014d). The presence of fibrous webs in these nonwoven polypropylene sorbents would come into view to be perfect materials for oil spill recovery because they enclose small pores which make easy haulage of liquid into the web and keep hold of the liquids after sorption. These sorbents are entirely diverse from the conservative textile fabrics. Praba Karan (2010) and Rengasamy *et al.* (2011) studied that polypropylene has finer diameter in contrast of kapok, milkweed, and cotton, and due to this finer diameter, it consists of smaller capillaries in its fiber assembly. From literature survey (Reed, 1999; Pasila A, 2014), it was found that the oil sorption by polypropylene is generally carried out through capillary connections between fibers, and this sorption possession is based on the pores obtainable between fibers.

2.5.2.7 Sheep Fleece Fibers

Oregon wool is not normally used in textile fabrication as it has short fiber length. On the other hand, wool is known as a naturally oil absorbent material that can absorb oil nearby 8–10 times of its weight (Reed, 1999). Maja *et al.* (2013) studied for sheep fleece that the possibility of using recycled wool-based nonwoven material as a sorbent in an oil spill cleanup. This stuff sorbed maximum quantity of base oil SN 150 than diesel or crude oil from the exterior of an artificial seawater bath. Surface modification of material with the pretreatment using biopolymer chitosan and low-temperature air plasma showed a slight decrease of sorption capacity. Fibers in loose form of the same source as nonwoven material have appreciably higher sorption capacities than examined nonwoven material. White light scanning interferometry investigation of the fibers recommended that unevenness of the wool fiber surface plays an important role in oil sorption and the laboratory trails showed that this material can be reused.

2.5.2.8 Kenaf

Kenaf is another cellulosic material readily available in some states. These natural sorbents have hydrophobic properties before any treatments due to their surface waxes. In modern decades, natural sorbents are manufactured from natural biomass such

as cotton (*Gossypium hirsutum*), kapok (*Ceiba pentandra*) (Karan *et al.*, 2011), Sisal (*Agave sisalana*), Coir (*Cocos nucifera*), loofa sponge (*Luffa cylindrica*) (Annunciado *et al.*, 2005), and Kenaf tree (*Hibiscus cannabinus* L.) (Shamsudin *et al.*, 2015). Kenaf is a plant that invented from Africa and the second most vital natural fiber subsequent to cotton, kenaf is an eco-friendly plant licensed by the Kyoto Protocol (Ahmad, 2010). The evaluation of kenaf-based sorbent properties in treating oil spills and waste water treatment are inadequate in the literature. Therefore, Shamsudin *et al.* (2015) found superior absorption value of Kenaf as compared to other fiber-based oil sorbents such as Sisal (*A. sisalana*), Coir (*C. nucifera*), and loofa sponge (*L. cylindrica*).

2.6 Recent Developments for Effective Water Cleaning

2.6.1 Porous Boron Nitride Nanosheets

As sorption is an effective method to clean up water, but frequently used absorbents like activated carbon materials (Lei *et al.*, 2013; Bayat *et al.*, 2005), manmade fibers, natural fibers (Deschamps *et al.*, 2003), and zeolites (Adebajo *et al.*, 2003) are having weak separation selectivity and squat absorption capacity. To beat these major drawbacks, a number of sophisticated materials have been developed and recommended.

Significant removal of oils, organic chemicals, and dyes from water is an important for environmental and water source defense (Dalton *et al.*, 2010; Aurell *et al.*, 2010). Advanced sorbent materials (Calcagnile, 2012; Zhu *et al.*, 2011; Sohn, 2012) with excellent sorption capacity have to be developed. It has been reported that the porous boron nitride nanosheets with very high specific surface area exhibit excellent sorption performances for a wide range of oils, solvents and dyes. The main features of these nanosheets are:

1. The oil sorption capacity of these nanostructured substrates is excellent and can soak up nearly 33 times of its own mass in crude oils and its solvents whereas resisting water.
2. As these boron nitride nanosheets have good resistance to corrosion, its cleaning and reusability is possible for further use to cleanup of spilled oil.
3. These sheets in the form of mats are also having the capability for water cleansing treatment because of their good recyclability.

All these uniqueness build these porous nanosheets suitable for a broad variety of applications in water purification as well as in oil cleaning also.

2.6.2 Carbon Nanofiber Aerogels

Over the past days, carbon-based aerogels (Wu *et al.*, 2014) have magnetized attention in a variety of fields like tools manufactured for power storage and adaptation, sensors, flexible conductors, and so many catalyst supports owing to its low apparent density, high electrical conductivity, porosity, and specific surface area (Aliev *et al.*, 2009;

Chen *et al.*, 2011; Kim *et al.*, 2012; Zhao *et al.*, 2012; Wu *et al.*, 2012). Various carbon-based aerogels, such as carbon nanotube (CNT) sponge (Gui *et al.*, 2010), spongy grapheme (Bi *et al.*, 2012; Zhao *et al.*, 2012), graphene/CNT hybrid foam (Sun *et al.*, 2013), and carbon nanofiber (CNF) aerogels (Wu *et al.*, 2013) have been used as sorbent materials for spilled oil. Very high sorption capacities, high-quality recyclability, and ecological friendliness are the special features of these aerogels. Yet, costly apparatus and composite skills involved for industrial applications. Zhen-Yu Wu *et al.* reported a new type of CNF aerogels which may also be used as well-organized sorbents for oil uptake with high sorption capability and brilliant recyclability. Significantly, in negative situations, these CNF aerogels can work smartly for cleaning of spilled oil as they can be potted even at a very high temperature like 400 °C.

Like porous boron nitride nanosheets, CNF aerogels are known for their excellent physical properties, *viz.* low density, high porosity, outstanding mechanical steadiness good hydrophobicity, and oleophilicity.

2.7 Test Methods for Evaluation of Oil Sorbents

2.7.1 Test Method for Oil Sorption Capacity

For laboratory test, take 1 g of material in dry form in an 800 mL glass beaker which is already containing 40 g of oil along with 400 mL of deionized water. In a laboratory shaker, shake this mixture at a frequency of 110 cycles/min for a time period of 15 min at 25 °C. According to standard test methods of ASTM International, USA (Standard test method (ASTM International, USA, 2007). A mixture of toluene and xylene (20/80 v/v) should be used as a solvent to determine the water content and this determination is known as the method of extraction and separation using efficient solvent like *n*-hexane, toluene, xylene, or any other economical combination. After that, the sample is usually detached from the conical flask with the help of a mesh and drained for 1 min. The following equation is recommended for calculating the oil sorption capacity (Q , g- oil/g- sorbent) of the sorbents.

$$Q = \frac{M_a - M_i - M_w}{M_d} \quad (2.1)$$

where M_a is the mass of the soaked sorbents after draining, M_i is the initial mass of sorbents, and M_w is the amount of water absorbed by the sorbent, and M_d is the fabric's dry weight.

The specialty of this test is that it can also be performed for sea water as well as without water (Figure 2.3). For dry system, place 50 g of sample oil in 1000 mL glass beaker followed by the immersion of a specific amount of sorbent in the prepared bath. A dry system encloses only crude oil. After trembling and draining the quantity of oil sorbed (S) (in g) per g of the sorbent is calculated using following equation:

$$S = \frac{W_{so} - W_s}{W_s} = \frac{W_o}{W_s} \quad (2.2)$$

where W_{so} is the mass of sorbent saturated with oil goods (g), W_s the mass of clean sorbent sample (g), and W_o the mass of oil substance retained into sorbent material (g).