Polymer Grafted Nanocomposites for Water Decontamination

Krishna Manjari Sahu, Swapnita Patra, and Sarat K. Swain

Abstract Polymer grafted nanocomposites have received high attentions from researchers for their versatile applications and amazing properties. The process of overcoming the contamination of water is one of the important application of nanocomposites prepared from polymer grafted matrix with reinforcement of nanostructurted materials. This chapter comprises of two impressive aspects. The difference between designing a polymer nanocomposite and polymer grafted nanocomposite and the eye catching changes in properties and applications by introducing grafting technique to polymeric nanohybrid materials is the first primary attraction of the present chapter. Secondly, by accounting the important exposure towards water treatment by different polymer grafted nanohybrid materials, this chapter gives a clear purpose for designing more potential polymer grafted nanohybrid materials by reaching the needs of the book. Different grafting mechanisms, along with the photocatalytic mechanism shown by polymer grafted nanohybrid materials are discussed. Dye adsorption, removal of metal ions, desalination of salt water and the antifouling behaviour of polymer grafted nanohybrid materials and membranes are detailed.

Keyword Polymer · Grafting technique · Nanocomposites · Water decontamination · Dye Adsorption · Desalination

1 Introduction

Water is a dominant renewable natural resource and is vital for living organisms present on the earth's surface. Population growth and rapid industrialisation are the major reasons behind the pollution of water. Although water is present in copious amount, human usable fresh water reservoirs are lesser in number. In addition, contamination of water with humongous number of pollutants such as heavy metals [1], dyes [2] and microbes [3] have degraded the quality of pristine water and as such, less amount of water is left for the usage of mankind. Since the need of fresh

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S. K. Swain (ed.), *Nanohybrid Materials for Water Purification*, Composites Science and Technology, https://doi.org/10.1007/978-981-19-2332-6_6

water is increasing day by day, saline water present in huge amount on the surface of the earth can be utilized as fresh water by the desalination process [4]. Treatment, purification and decontamination of wastewater processes are not restricted to single method. The recuperation of drinking water from wastewater is a difficult and laborious process with multiple purification techniques. Commonly, there are three steps that can be employed for purification and decontamination of water, primary, secondary and tertiary water treatment. Primary water treatment process involves the removal of suspended particles and various micro pollutants through microfiltration, coagulation and chemical precipitation methods. In case of secondary wastewater treatment, naturally originated microbes play a crucial role as they have the potential to degrade chemical pollutants into eco-friendly molecules that results in lowering of negative influence on ecosystem. Tertiary water treatment process is applied to eradicate pollutants found in water even after primary and secondary purification process like monovalent ions. In order to enhance the quality of water and to make available recycled water for irrigation and industrial purposes, different materials and techniques for water purification have been proposed. Out of those, the materials which have large number of pores, high surface area and adsorptive capacity, are preferred by the researchers for advantageous outcomes [1].

1.1 Nanoparticles

Nanoparticle (NP) is an ultrafine unit with dimensions measured in nanometer and its size ranges between 1 and 100 nm [5]. The possibility to explore substance at nanoscopic range has created several opportunities to investigate NP as a principal material in water purification technique. NPs are superior to larger scale particles in various means such as high surface area, considerable electrical and magnetic properties [6]. The basic layout of nano ranged particles of a substance is mainly governed by the constituents of parent substances, atoms present within the certain area of material and the types of interaction among atoms. Based on chemical composition and chemical interaction, now-a-days, NP has been used in sundry applications such as biomedical field, food packaging, sensor and mainly in water purification treatment [7–9]. On account of distinct physical and chemical properties, metal NPs have gained much attention in recent decades in different science fields such as chemistry [10], physics [11] and material science [12]. Different NPs have been thoroughly examined and adapted in various medical applications such as wound dressing and antimicrobial coatings. Material that encloses the NPs steadily released NPs at a slower rate to provide protection against bacteria. Since NPs have considerable amount of high surface to volume ratio and high surface energy and also show excellent protection against bacteria, it can be used in fabrication of polymer composite material for the removal of microbes from sludge water [13].

1.2 Polymer Nanocomposite (PNC)

A composite is fabricated from two or more distinctive materials which are on mixing formed a stronger substance than those of individual materials. The constituent substances do not fully blend or lose their individual integrities; they mix and provide their felicitous characteristics to enhance the quality of the final product. Composites are multiphasic system, generally have two phases, one is matrix phase and another one is dispersed phase. Nanocomposite is defined as the composite consists of nanoscale material which is about 10 –100 nm at least in one phase. Nanoscale particles which are broadly used in fabrication of nanocomposite are nanotubes or lamellar nanostructure. Nanocomposites are synthesized by combining two or more components: one component must be used as dispersed phase and another is used as matrix phase. The substance which can be used as dispersed phase are allotropes of carbon, nanocluster, oxides of inorganic materials or semiconductors and organic polymers or organic and organometallic compounds whereas different bio molecules such as amino acid, protein, sugar, enzyme and sol–gel derived polymers are used as matrix phase. In agreement with the materials used as matrix, for instance ceramic, metal and polymer, nanocomposites are classified into three categories. PNCs can be engineered by the combination of a polymeric matrix and usually, inorganic nanomaterial as discontinuous phase [14]. This type of nanocomposite is also called hybrid nanocomposite. Inorganic materials such as TiO_2 [15], SiO_2 [16], ZnO [17] and Ag [18] with outstanding features are dispersed in a polymer matrix for obtaining composite. PNCs among several nanocomposites are the prominent materials of present research, investigation and development not only in industrial field but also most importantly in environmental pollution reduction and biomedical field. Different aspects of PNC such as active functionality, capable of forming film and ability to very its constituent dimension, makes PNC a foremost material to use in removal of various organic and inorganic effluents form wastewater to make water reusable. In recent times, PNC grows as a dominant material for industrial waste removal from various polluted water bodies because of its production friendly, lightweight, mechanical strength and most importantly high adsorption ability [19]. Several applications exhibited by PNCs are schematically represented in Fig. 1.

1.3 Grafting Technique

Polymer is defined as a high molecular mass compound obtained by polymerising repeating units i.e., monomers. Typically, polymers can be categorized into two different types such as homo-polymer and copolymer, based on number of repeating units used as reactants during the synthesizing process. The former type of polymer is the combination of similar type of repeating constituents whereas second type of polymer is engineered by using two dissimilar types of repeating units. According to the structure of polymer, it can also be classified into three types such as linear,

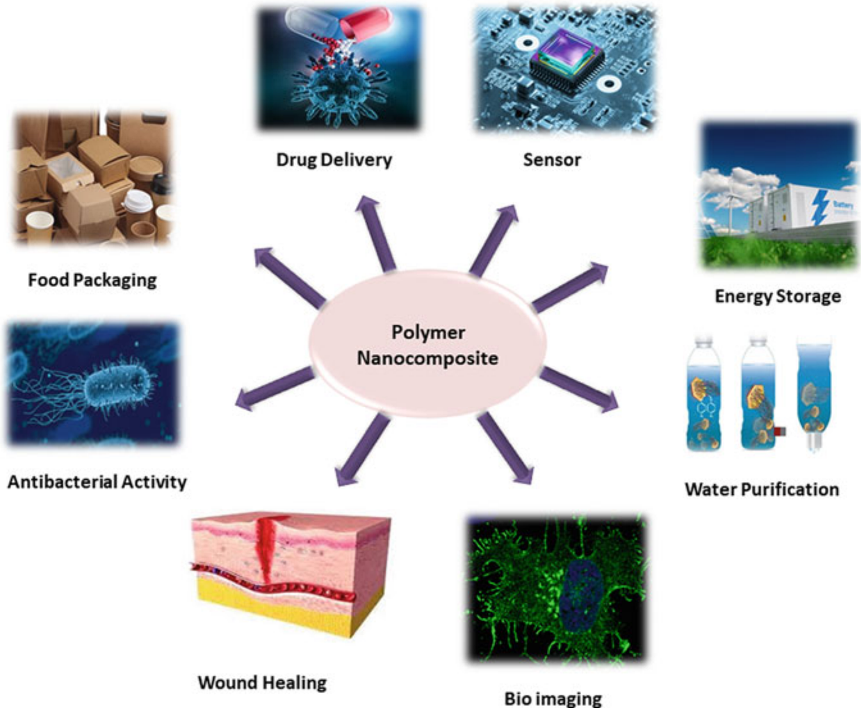

Fig. 1 Schematic representation of various applications of PNC

branched and three-dimensional network polymer. The monomers are linked together in a straight-line fashion to form linear type of polymer. Branched polymer generally consists of two parts; linear main chain and another one is branching unit that attached to the main chain through covalent bond. The polymers, in which branching fragments or parts are connected with the primary chain, are called graft polymers. To prepare graft polymers, researchers mainly follow three kinds of grafting methods such as "grafting to", "grafting from" and "grafting through" techniques. In case of "grafting to" polymerisation approach, branching polymer unit must contains a reactive end group which has to react with different functional groups present on the principal polymer chain while in case of "grafting from" approach, the formation of branching begins on the surface of primary polymer chain due to the presence of reactive initiating sites on the surface of backbone. In "grafting through" preparation method, one polymer unit containing reactive site group copolymerized with another monomer unit. Addition of branch side chain can be done during the synthesising process or after the formation of the principal chain. The property of graft polymer depends on grafting time with relation to number of graft side chains. Some specific types of surface material that can be used as backbone for the fabrication of graft polymer are manmade polymers, naturally occurring polymer and metal. Metal surface does not contain any reactive sites, so modification of metal surface is one of the mandatory steps to introduce functionally active sites. This also helps to make metal surface a favourable synthesising base for the preparation of grafted polymeric materials. The frequently used polymerisation technique for the fabrication of grafting polymer is free radical polymerisation [20].

1.4 Polymer Grafted Nanocomposite (P-g-NC)

Grafting technology is not limited to the formation of polymer only; instead, it has further applications in the fabrication of numerous advanced materials related to polymer, like PNC with extraordinary properties. The three grafting mechanisms used during the synthesis of PNCs are illustrated in Fig. 2. Generally, PNCs that are engineered through grafting methodology are considered as polymer grafted naocomposites (P-*g*-NCs). P-*g*-NCs contain polymer brushes and these brushes help nano ranged particles to disperse evenly throughout continuous phase of P-*g*-NCs. Polymer brushes have two parts: one is centre or core part that contains NP and

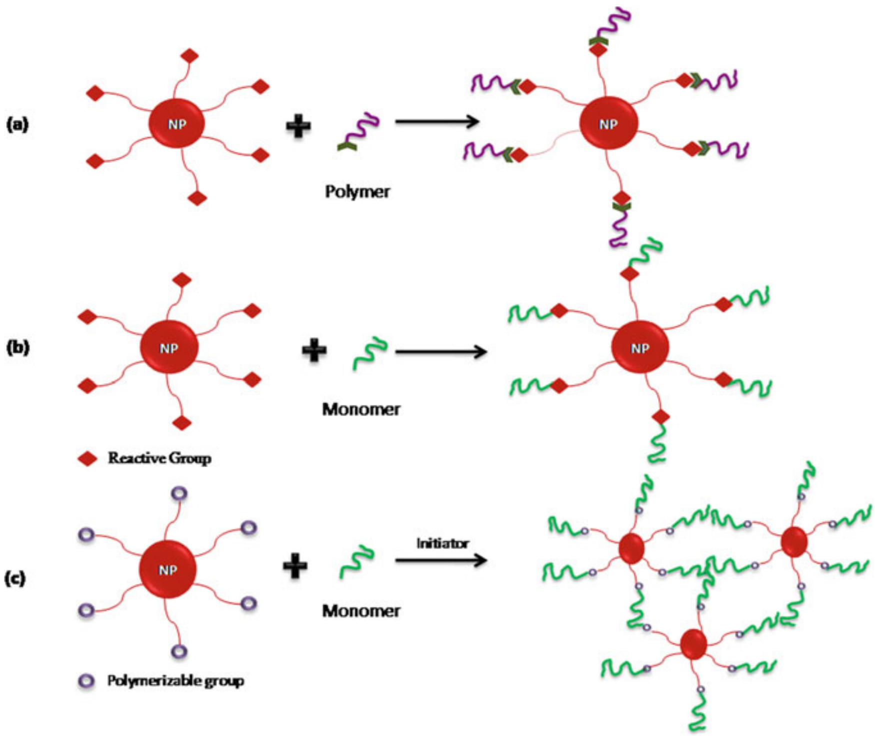

Fig. 2 Schematic representation of **a** "grafting-to" **b** "grafting-from" **c** "grafting-through" mechanism

other one is the polymers contained part that surrounds the central NP. Nanoscopic particles with unique functionality such as iron NP that has magnetic property, gold NP that has optical property or the intricate nanomaterials like virus, protein, caspid etc. can be used as central part of polymer brush. Preparation of P-*g*-NCs depends on several factors, such as types and number of functional groups present on repeating units and most importantly magnitude and uniformity of grafting on the surface of core part. Polymers used for grafting allow controlled distribution and assemblement of NPs during the P-*g*-NCs formation. Maximum outcomes have been shown by the polymer brushes that deprive of crowded grafted polymer on nanosized particle since repulsion among polymers decreases the stability of material. The particular polymer used in preparation of P-*g*-NC and its properties decides the employment of P-*g*-NCs in various application fields e.g., poly (methacrylic acid) can be used in drugs administration applications where as poly (ethylene glycol methyl ether) can be used in preparation of battery. NPs exhibit two types of charge distribution inside the atoms: one is uniformly distributed charge system and another one is direction-oriented dipole. Distribution of charged density inside the NPs governs the 2D structure of nanomaterials but this factor does not affect the entire structure of P-*g*-NCs. For example, silica NPs possess uniform charged density and have isotropic core-core interactions whereas magnetised iron NPs contain dipole, so isotropic core-core interactions are not found in iron NPs contained materials. The structure of P-*g*-NCs that have polymer brushes with same degree of polymerisation show random orientation of polymer brushes in sparsely grafted polymer brushes reign [21].

The involvement of grafting approach in the preparation process of P-*g*-NCs has significantly contributed in enhancement of properties such as absorption, photo-catalytic and mechanical stability. Adsorption phenomenon follows two types of adsorption mechanism; physical and chemical adsorption. Physical adsorption is the result of various intermolecular forces such as hydrogen bonding, electrostatic interaction and Van der Waals force of attraction between adsorbent and adsorbate whereas chemical adsorption is occurred through the formation of chemical bond between the reactive sites present on the surface of both adsorbent and adsorbate. Traditional adsorbents that are used for the purpose of water treatment exhibit poor adhesion capacity since this kind of adsorbents contain only few physical active adsorption sites and also the result of chemical adsorption is not so impressive. Owing to the above facts, researchers are more interested to do fabrication and investigation related to novel P-*g*-NCs with a greater number of adsorption sites [22]. P-*g*-NCs have shown various improved properties such as mechanical and thermal stability and catalytic behaviour as compared to PNCs those are formed by techniques other than grafting method. P-*g*-NCs have notable adsorption capacity, because it comprises of NPs which have surface area more than the bulk materials. Also, the addition of nano ranged particles into the matrix of polymer through grafting technique has extremely enhanced the adhesion ability of different molecules on the surface of adsorbents since grafted sites provide additional surface area. During the purification process of water by adsorbent, the major challenge that many researchers have faced is the pollution caused by secondary pollutants. To resolve the secondary pollutants problem, recently researchers have prepared P-*g*-NCs that are able to remove different level of pollutants. Photocatalytic property of a functionalised surface is depend upon on the functional groups and its oxidative ability. P-*g*-NC contains various light responsive functional groups and the free electrons of nanosized particles help in initiation of reduction and oxidation processes to degrade numerous organic effluents into environment friendly molecules as illustrated in Fig. 3. Due to the above reasons, P-*g*-NCs exhibit excellent catalytic property [23]. Another governing character of P-*g*-NCs is mechanical stability. The degree of mechanical property of a composite material is usually determined by the mechanical strength of constituent materials and the interaction present between continuous and non-continuous phase. So, P-*g*-NC shows improved mechanical property compared to its constituent materials i.e., polymer and NP. In case of P-*g*-NCs, the mode of dispersion of nano ranged particles in matrix continuous phase plays a vital role in determining the extent of mechanical stability. The most advantageous method to acquired maximum mechanical outcome is to use grafting methodology in the preparatory process. Giovino et al. has shown the marvellous mechanical stability of P-*g*-NCs by synthesising silica-polystyrene composite. They have prepared a silica grafted brush by alternating the surface of silica using styrene polymer and then dispersed these brushes into polystyrene continuous phase system [24]. Figure 4 shows different eye-catching properties of P-*g*-NC.

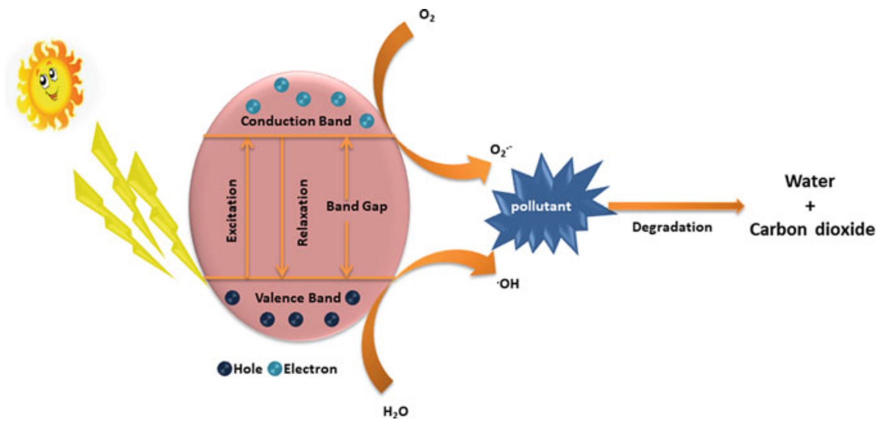

Fig. 3 Schematic illustration of photocatalytic mechanism shown by P-*g*-NCs

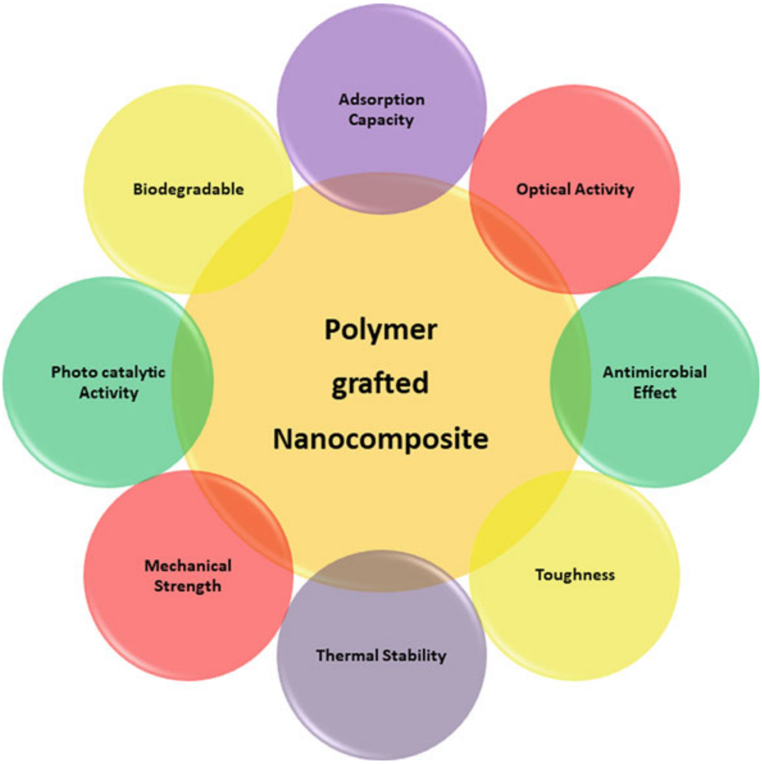

Fig. 4 Schematic representation of properties of P-*g*-NC

2 Approaches Towards Water Decontamination by P-g-NCs

2.1 Dye Adsorption

Dye has been used to give materials some astonishing shade of colours since ancient period of time. Unlike synthetic dyes, natural dyes are easily dwindling away on expose to sunlight and washing. With enhanced colour retaining property than those of natural dyes, synthetic dye is first developed by WH Perkins in 1896 to use in textile industries as well as in food industries for impartation of colour on substances. Industry in which synthetic dyes are used as raw materials releases huge amount of environmental toxifying wastewater to the nearby fresh water reservoirs. Dye contains colour showing units like auxochromes and chromophores which also give stability to the structure of synthetic dyes and make degradation of dyes more difficult. Due to the above reasons, removal of harmful dye pollutants from various water bodies is one of the most challenging tasks in water purification process.

Recently, thousands of scientists have already investigated and proposed sundry kinds of method such as biological, chemical and physical methods to extirpate dye from wastewater [25].

2.1.1 Biological Dye Removal Method

Among several types of dye removal methods, biological dye degradation method is a paramount method since the chances of release of secondary pollutants is negligible. Biological and chemical methods are mainly implemented to eradicate colour from the wastewater by detaching colour adding chromophore fragments from dyes. The standard biological methods used for this purpose are aerobic and anaerobic processes. During aerobic degradation method, oxygen hinders degradation process because of its high reduction potential value and electron accepter property. Owing to the above fact, the besmirching of coloured wastewater containing azo dye like Reactive Orange 16 is preferred anaerobic environment. Another effective biological dye degradation process is bioremediation. This process is implemented to decontaminate wastewater containing large number of organic pollutants. The wastewater release from different textile industries contains hazardous pollutants mainly azo dyes, pesticides and derivatives of phenol. The effectiveness of bioremediation process depends upon the capability of microbes to withstand in such adverse environment [26].

2.1.2 Chemical Dye Removal Method

Like biological dye removal method, chemical dye removal method is also used in the process of besmirching of organic effluents but the pathway followed for degradation mechanism is different for each case. Chemical dye degradation method includes photocatalytic process, electrochemical reduction, and reduction by Fenton's reagent. The main component for photocatalytic degradation under UV radiation of different colorants is hydroxyl free radical ($\cdot OH$). Including hydroxyl free radical, other reactive species such as superoxide (O^{2-}) and hole (h^+) promote the breaking of covalent bond to convert organic contaminants into less toxic substances through oxidation or reduction mechanism [27]. Fenton's reagent is another efficacious chemical reagent which is useful in degradation process of dye. This reagent contains hydrogen peroxide and ferrous ion which are responsible for the degradation process to treat various organic pollutants. In this dye removal process hydroxyl radical plays an important role as it has strong oxidative capacity. The reusability characteristic of this reagent makes the entire process economical [28]. Electrochemical reduction process is another notable pollutant degradation method in which metals are used as catalytic system. Different organic pollutants such as azo dyes and phenol containing pollutants have been eliminated from wastewater by using electrochemical reduction process [29].

2.1.3 Physical Dye Removal Method

The mainstay of physical dye removal method is adsorption that includes both physical and physiochemical adsorption method. This method involves the direct eradication of organic and inorganic effluents through composites or any other materials with good adsorption capability. Dyes can be of various types but for the eradication and degradation, the material that are used during purification process is depend upon the charges present on dyes. The cationic dyes require negatively charged material on the surface of adsorbent and vice-versa. Physical method is eminently convenient, since this method uses no living organism and less amount of chemical is required as compared to other methods [30]. Different biological, physical and chemical methods for dye eradication have been illustrated in Fig. 5.

Grafting technique has been introduced during the synthesis process of numerous hybrid materials to enhance the adsorption ability. Singh and Dhaliwal have fabricated AgNPs/GG/Poly(AA) based on silver NPs. They followed in situ preparation technique for the incorporation of silver NPs onto the graft copolymer made up of acrylic acid and guar gum. This nanocomposite is one of the competent adsorbent materials for effluent eradication, since the diffusion process by which dyes are adsorbed onto the material is an endothermic and spontaneous process. The NPs used in this process provide high surface area to the adsorbent for better binding ability [31]. Many materials with high adsorption potential are used in the process of

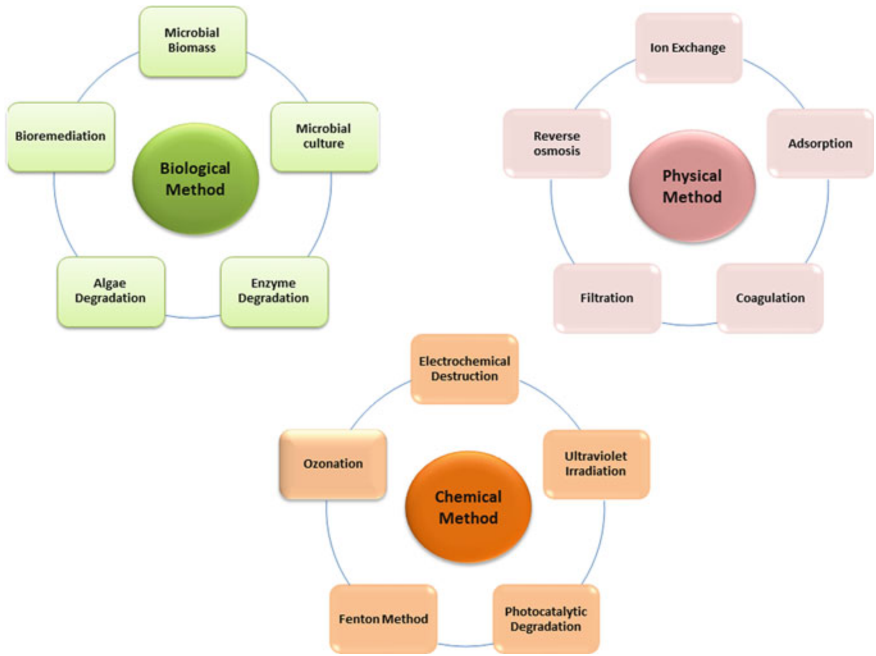

Fig. 5 Schematic illustration of biological, physical and chemical dye removal method

decontaminating water. Among those kinds of materials, hydrogel with promising adsorption capability is one of the prominent materials that have been used as adsorbent for the purification of polluted water releases from different textile industries. For the fabrication of above kind of material, biodegradable resources have attracted the attention of many researchers since these materials are less toxic and environmentally friendly in nature. Hydrogel can be synthesised by using different kinds of polymeric material. But in view of above fact, now-a-days biodegradable polymeric materials have been used in the fabrication of hydrogel nanocomposites for low production of secondary pollutants. The best known biodegradable polymeric materials are polysaccharides. Mittal et al. has engineered polysaccharide based GK-cl-P(AA-co-AAM)/SiO_2 hydrogel nanocomposite for the adsorption of methylene blue (MB) dye. This P-*g*-NC material is based on environmentally friendly polymer gum karaya (GK). At first, the matrix is prepared by grating GK onto the other two polymers: poly acrylic acid and poly acylamide. Silica nanoscopic particles have been loaded to the polymer matrices by in situ preparation method [32]. Jing et al. has investigated the effectiveness of grafting on adsorption capacity of P-*g*-NCs by preparing Lys-PGMA@Fe_3O_4. The magnitude of grafting of poly(glycidal methacrylate) (PGMA) brushes on the surface of Fe_3O_4 NPs increases with increase in polymer formation. The prepared P-*g*-NC is a pH responsive material and due to this, it is able to absorb unlike charged dye at different pH concentration levels. Experimental findings revealed that lemon yellow (LY), a negatively charged dye shows higher adsorption ability at lower pH concentration value (pH = 4.0) whereas MB, a positively charged dye has high adsorption capacity at higher pH level (pH = 10.0). The fabricated system has the adsorption capacity for LY and MB is 0.54 and 0.85 $mmol \cdot g^{-1}$, respectively. One of the greatest advantages of using magnetic NPs in the preparation of P-*g*-NC is that it can be easily separated out from liquid after the purification technique by the use of magnetic field [30]. Kulal and Badalamoole have investigated the eradication of dye and heavy metal by fabricating a Ggh-g-PAcM/Fe_3O_4 P-*g*-NC hydrogel materials using magnetic NPs. The adsorption capacity of the nanocomposite hydrogel is much higher than normal hydrogel since the addition of NPs, fill up the free space present within the hydrogel. As a result, the surface area of the prepared materials increases. They have also studied the adsorptivity with respect to concentration of iron NPs and they concluded that the capacity of the adsorptivity increases with increase in the concentration of NPs but up to a certain limit. The prepared materials have shown excellent property in removal of bivalent heavy metals and cationic dyes. The adsorbent also showed excellent reusability property [33].

Hydroxyapatite is a nature originated mineral and has shown its essentiality and need as constituent material to repair bone. It exhibits biocompatibilty nature since it is one of the important compositions of bone and teeth. This naturally occurring biopolymer has largely been use in the application of detoxicfication of organic effluent like dyes because of strong interaction between the hydroxyapatite and dye molecules. Graphite oxide (GO) also able to capture dyes from industrial polluted water due to the presence of functional reactive groups on the surface of GO. Hosseinzadeh and Ramin have fabricated a hydrogel i.e., starch-graft-poly(acrylamide)/grapheneoxide/hydroxyapatite for the successful eradication of malachite green (MG) organic effluent. The major reasons behind the eradication of dye are the anionic charged surface of fabricated nanocomposite hydrogel and the interactions occurred between the functional groups present on nanocomposite and the cationic charged present on MG dye [34]. Other naturally occurring mineral in nanoscale range is palygorskite, a combined form of hydrated magnesium, aluminium and silicate minerals. Surface modification by means of chemical and physical approaches shows significant change in adsorption property of palygorskite mineral. AL-Hammadi et al. has synthesized a material by grafting poly(trimesoyl chloride-melamine) on the surface of palygorskite (PTMP) for dye and heavy metal eradication from water effluents. The prepared material has shown effective removal of MO and heavy metals like nickel, arsenic, mercury, cobalt, molybdenum and chromium [35].

2.2 Metal Ion Removal

Contamination of water by metal ions is one of the major reasons that put harmful impacts on ecosystem and also the consumption of hazardous heavy metal contaminated water imbalance immune system of human body. Heavy metals are generally exposed to water reservoirs due to the extraction of metals from its respective ores, from the industries that employ heavy metals as raw material for the manufacturing of products and from agricultural wastewater. Unlike dyes, heavy metals are inorganic effluents but the techniques and materials use for eradication process are similar to organic effluents up to some extents. Adsorbents are primarily divided into two types such as traditional and non-conventional. Non-conventional materials are based on naturally originated materials and are significantly more preferable than traditional one because of their nonimmunogenic, noncarcinogenic and non-toxic nature. The functional groups present on the biopolymer have the potential to formed chelated metal ion complexes with heavy metals ion present in contaminated water. Owing to the above facts, introduction of biopolymer as one of the preparatory material for the synthesis of adsorbent has gained attention of numerous scientists who have been devoted to research area based on water purification treatment related to heavy metal elimination [36]. Sodium alginate (Alg) has the suitable characteristics to form gel by reacting with several cross linkers. Mittal et al. has studied the adsorption of Pb(II) and Cu(II) by fabricating PMMA-g-Alg/Fe_3O_4 adsorbent using oxidative free radical grafting polymerisation technique. The adsorption of Pb(II) and Cu(II) by the synthesised material is found to be 62.5 mg g^{-1} and 35.71 mg g^{-1}, respectively [37]. Hexavalent chromium ion is considered as one of the most life threatening heavy metal since it has the ability of oxidise the bio molecules present in living organisms. Among biopolymers, Chitosan is the predominant one due of the presence of hydroxyl and amine groups which play an important role in adsorption of heavy metals by generating interactions between functional groups and heavy metal ions. Sharma et al. has fabricated chitosan and N-isopropylacylamide based P-*g*-NC and investigated selective elimination of various heavy metals such as chromium(II), iron(II), lead(II) and chromium(IV) [38]. Another heavy metal that generates negative influence on environment by polluting fresh water bodies is mercury. Recently, researchers have specified the mercury metal ions as a perilous pollutant because it has the competence to create harmful effects within the organisms by entering food web. The disclosure of mercury into the surroundings is mostly because of mining, paint and pharmaceutical industries. According to HASB theory, mercury comes under the soft acid category, so it needs soft base categorized functional groups to form bonds. Since papain contains four sulfhydryl functional groups as responsive sites to interact with metal ions, papain matrix can be employed for the removal of mercury. Metin and Alver have prepared a papain chitosan/clay composite bead using graft polymerisation technique to polymerise methacrylic acid and studied the selective adsorption of mercury ions in presence of other metal ions [39].

The extensive use of non-renewable resources for energy production has dwindled the number of resources but escalated the magnitude of habitat pollution. Due to the above reason, mankind has been forced to use nuclear energy as an alternative. The major reason for disclosure of radioactive metals into the fresh water reservoirs is nuclear power plant. Magnetic NPs have been predominantly used as surface area enhancer for adsorbent species because the magnetic property helps in easy separation of NPs loaded adsorbent after the treatment of wastewater. Bayramoglu and Arica have studied the selective adsorption of U(VI) ions with other poisonous metal ions from water by synthesised a silica coated magnetic nanoranged particles grafted with polymer [40]. Elsaied et al. has fabricated a super adsorbent composite by using derivative of cellulose and magnetic iron NPs with other polymers to entrap radioactive metal ions, namely Cs^{+}, Co^{2+} and Sr^{2+} [41]. A number of P-*g*-NCs with their applications and characterization methods are summarized in Table 1.

2.3 P-g-NC as Antifoulant

Eradication of microorganisms from contaminated sewage water is the most crucial step in wastewater treatment process. Predominantly numerous filtration techniques have been employed for the detoxification and purification of municipal and biomedical wastewater. Filtration process is a result of uprising research based on technology of membrane. This method has manifested highest involvement and considerable efficacious results without adding any ancillary chemicals during the water purification processes. Various type of membranes has been grouped into two main categories i.e., polymer based membrane and inorganic based membrane. The former type of membrane is widely used as a filtration medium because it contributes substantially high thermal, mechanical properties, ease of water permeability, greater fouling property and most influentially membrane forming potential than inorganic based membrane. Polymer based membranes technologies are generally classified into four categories on the basis of recuperating filtration method and diameter of pores

Table 1 A summary of different P-gNC_s investigated for dyes and heavy metals eradication along with their characterization methods

SI. No	Polymer grafted nanocomposites (P-*g*-NCs)	Characterization/Properties	Application in eradication	Pollutants	References
1	Chitosan-g-acrylic acid/SiO_2 hydrogel	FTIR, TGA, SEM, Inductively coupled plasma mass spectrometry	Heavy metal	Co(II),Cu(II), Pb(II) and Zn(II)	[42]
2	Poly(AMPS)-g-GT/GO hydrogel	FTIR,FESEM, EDS, XRD,TGA	Heavy metal	Pb(II), Cd(II), and Ag(I)	[43]
3	Fe_3O_4/PMA-g-PVA	FTIR, TGA, SEM, XRD	Heavy metal	Ag(I), Ni(II), Cd(II), Pb(II) and Co(II)	[44]
4	Poly(acrylamide)-g-chitosan@γ-Fe_2O_3	FTIR, SEM, EDS, XRD, TEM,UV–Vis	Dye	Malachite Green	[45]
5	Dext-g-PMA/SiO_2	FT-IR, ^{13}CNMR, SEM, EDAX, XRD	Dye	Methylene blue, Crystal violet and Methyl orange	[46]
6	Chitosan-grafted-polyaniline/Co_3O_4	FTIR, FESEM, TEM, XPS, XRD, TGA, UV–Vis	Dye	Methylene blue	[47]
7	k-carrageenan-g-poly(meth acrylic acid)@ Fe_3O_4 hydrogel	FT-IR, XRD, SEM, TEM, VMS	Dye	Crystal violet	[48]
8	Gum xanthan-grafted-polyacrylic acid@ Fe_3O_4 Hydrogel	FTIR, XRD, TEM and SEM–EDS	Dye	Methyl violet	[49]
9	GA-cl-PAM/ ZnO Nanocomposite	FTIR, SEM, TGA, XRD	Dye	Malachite green	[50]
10	Gum ghatti (Ggh) and 4-acryloylmorpholine (AcM) @ Fe_3O_4	FTIR, TGA, XRD, SEM, BET, VSM	Dye and Heavy metal	Methylene blue, Rhodamine 6 G, Cu(II) and Hg(II)	[33]

present on membranes: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). Among the above mentioned membranes, MF has porosity level with pore diameter ranging from 1 to 0.1 μm while RO has the least porous structure, possessing pore size less than 0.0001 μm. Depending upon the porosity level, membranes are used in different level of water treatment process to filtrated distinct pollutants. For instance, metal ions with one valence electron are separated by NF method. The filtration process, by using above four membranes depends upon the pressure applied on polluted liquid while passing through membrane. The process by which foulants get accumulated on the upper layer or within the pores present on solid material is called fouling. One of the serious problems that membrane technology has encountered is the accumulation of pollutants on surface of membrane which first leads to slowdown and then gradually occludes liquid flow through membrane. Due to the above facts, reusability capacity of film decreases and the process become less economical. Depending upon the foulant types and characteristics, various fouling membranes are being synthesised for water purification purposes. The avoidance of fouling caused by several microbes is one of the major strenuous processes since the number of bio-pollutants greatly increased due to the nutrients present on polluted water. Except the eradication of biofoulants, all other foulants removal through adsorption process is reversible in nature. Fouling property depends upon the hydrophilic and hydrophobic nature of materials that are used in the preparation of membrane. The membrane with high hydrophobic capability has its greater fouling ability towards organic wastewater release from industries. Many of nanoranged particles like silver, titanium oxide has shown outstanding performance in the removal process of biofoulants like bacterial because of their antibacterial characteristics against both gram positive and negative bacteria. The success rate of foulants adsorption is significantly improved by using nanocomposite membrane during the purification process [51]. Incorporation of NPs onto the matrix of polymer provides greater antifouling ability. But, due to the lack of stability, the NPs start to agglomerate and the dispersion of NPs is not uniform throughout the polymer matrix. Such kind of problem has been successfully avoided by grafting the surface of nanoranged particles with suitable polymer using reversible addition/fragmentation chain transfer technique. Also, the roughness present on surface has shown great proficiency on the performance of the membrane during the filtration process of polluted water. Rafiei et al. has reported that the anti-fouling properties of PVDF/PVP-g-TiO_2 thin film P-*g*-NC is greater than polyvinylidene fuoride (PVDF) membrane because of the high surface area and roughness [52]. The bacteria, having harmful effects on living organisms are called pathogen and are mainly responsible for water borne diseases. P-*g*-NCs are also used in water disinfection process to remove pathogens. Photocatalysis is one of the impressive characteristic that a NP possesses. TiO_2 NPs hold the capacity to harm cell wall of bacteria with the help of oxygen reactive species by utilizing solar energy as a source. Wang et al. has studied the photocatalytic effect of prepared Fe_3O_4@TiO_2 /glycopolymer nanocomposite. Above prepared material has the capability to encapsulate and damage of E.coli bacteria by rupturing the cell membrane [53]. The rupturing and damage of a cell are demonstrated in Fig. 6. Certain specific type of materials, with required hydrophilic environment, is needed

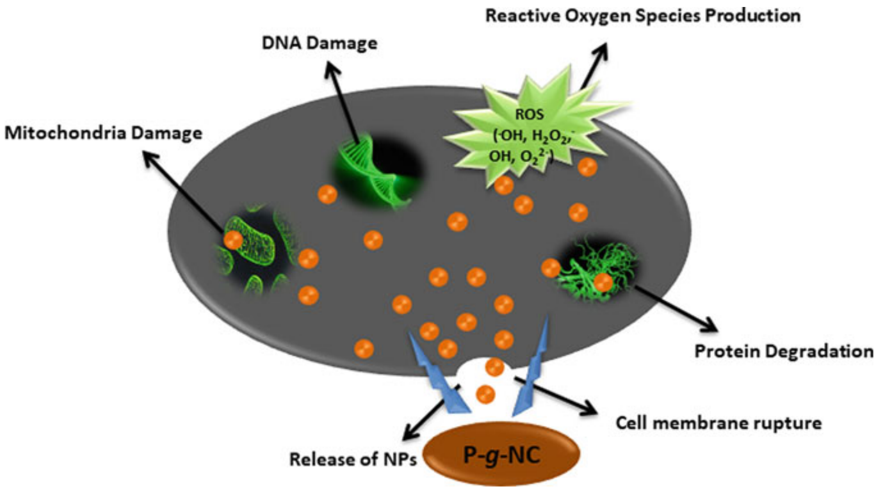

Fig. 6 Schematic representation of antibacterial activity shown by P-*g*-NCs

for the capturing of microorganisms inside the P-*g*-NCs. Hydrogel is suitable for this type of application due to the availability of pores for the entrapment of microbes. The functional groups present on GO surface have the high magnitude of adsorption capacity of pollutants by interacting with polymer. Glutamic acid (Glu) is a well-known eco-friendly and biocompatible material. Yu et al. has synthesized PVA/GO-Glu hybrid hydrogel nanocomposite beads by grafting the polyvinyl alcohol (PVA) onto the GO-Glu surface. This material shows greater loading capacity of microbes due to the enhanced size of pores present on PVA matrix [54].

2.4 Desalination

Sea and ocean hold water more than 95% of total earth's water but this kind of water has no utility in daily use of human and for industrial purposes. In view of the above reason, researchers have been focused their interest on desalinating and purifying sea water. Generally used methods for purification of saline water are distillation, multi-stage flash and electrodialysis. The extensively employed method for the purification of desalinated water is RO because this process has low cost and low energy consumption value. The most preferable material for this process is polymeric thin film composite with property enhancer nanoscopic particles incorporated within it. In last decades, researchers are more fascinated into the fabrication of membrane that capable of performing in a long-term basis and have the characteristic of low negative impact on surroundings. Forward osmosis has the cardinal importance for the purification of saline water as it overcomes certain disadvantages such as high energy consumption, less antifouling ability, less reusable capacity of membrane and expensive raw material demand [55]. β-cyclodextrin is a hydrophobic cavity containing oligosaccharide polymer. The property of β-cyclodextrin is augmented by functionalized it with GO for water treatment application. Matshetshe et al. has fabricated a thin film i.e., β-CD-f-GO/PA with greater antifouling, desalinating and antimicrobial property [56]. Bagheripour et al. has fabricated PES/PAA-Fe_3O_4 NF membrane by using immersion precipitation method and casting solution technique. Magnetic iron NPs are first grafted with poly acrylic acid to form polymer brushes and then distributed uniformly in matrices of polyethersulfone (PES). The grafted brush is used as a filler to enhance hydrophilic attraction between membrane and pollutants. They concluded that the porosity and water permeability through the prepared P-*g*-NC membrane are increasing with increase in loading of polymer brush upto 0.5%wt [57].

3 Conclusion

Treatment, purification and disinfection of wastewater are the need of hour to fulfil the demand of fresh water. Degradation of dye, eradication of heavy and radioactive metals, removal of pathogenic bacteria and desalination of brackish water are the most important applications in water purification process. By changing fabrication procedure with simple inclusion of grafting method such as "grafting to", "grafting from" and "grafting through" has shown extraordinary outcomes of P-*g*-NCs than the PNCs formed by conventional process. Out of wide varieties of materials, P-*g*-NC is the best potential candidate for this application because of its pronounced adsorption ability, notable photocatalytic behaviour, remarkable antibacterial property and exceptional mechanical and thermal stability. P-*g*-NC has been successfully implemented and investigated its predominance in various wastewater purification processes not only at laboratory level but also at commercial level.

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