NANOCOMPOSITE HYDROGELS AND THEIR APPLICATION FOR ENVIRONMENTAL REMEDIATION: IN REVIEW

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Abstract

Over the last years, nanotechnology has been implemented in almost all branches of human live. Until now, numerous nanomaterials have produced and used to eliminate inorganic and organic species from wastewater effluents, in many cases, these are found more efficient than the conventional adsorbents. Within these attempts, hydrogels as a group of polymeric materials have received high interest in recent years. The hydrophilic structure of which renders them capable of holding large amounts of water in their three-dimensional networks. The extensive employment of these products in a number of industrial and environmental areas has considered being of prime importance. In this paper, the fundamental concepts, classification, physical and chemical characteristics, production methods and technical feasibility of their utilization is reviewed based on the composite hydrogel. A special attention has given to utilization of them for wastewater purification especially for the effluent received from textile industry.

1. Introduction

One of the extremely major problems facing the modern world is the shortage of natural resources and the environmental pollution resultant from industrial activities. There is no doubt that water is an important natural resource and it needs protection. However, rapid industrialization and urbanization since 1940's has continuously reduced the quality of water due to the addition of large amounts of pollutants such as pesticides, petroleum hydrocarbons, heavy metals, polychlorinated biphenyls, and synthetic dyes to the receiving environment [1]. These necessities to innovate among traditional techniques to be able to apply efficient processes in such a way that contaminants can be removed or even recovered to be reincorporated into productive processes [2]. Although, several physical, chemical and biological treatment methods have been developed and successfully adopted in to the industry to solve this problem, in recent years, adsorption technique has been re-gaining interest due to its own advantages on the removal of stable pollutants, flexible process design, process economy and capability of effectively removing heavy metals at very low concentration (1 – 100 mg/L) [3]. In adsorption, one of the key parameter that influences treatment recovery is the adsorbent

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material. Therefore, adsorbent materials are of great scientific and technological interest owing to their ability to interact with specific substances and efficiently separate them from a mixture. Among the materials that have been practiced as adsorbents, the inorganic particles and polymers / biopolymers are the most preferred materials. Most of them have acceptable adsorbent capacities on their own, but recently, the generation of polymeric matrices in the form of hydrogel reinforced with inorganic materials or mixtures of polymeric networks has been explored as innovative material to improve or increase the adsorption capacity. Composite hydrogels combine effective adsorption, high specific surface area and easy applicability, so they represent a great alternative for the elimination of heavy metal ions or organic substance present in aquatic ecosystems [**3**].

Within the well-known pollutants, heavy metals and perfluoroalkyl substances or organic dyes are representing major contaminant. Dyes have been linked to a variety of health problems in humans and aquatic life. Various industries such as textile, leather, paper, cosmetics, medicine, and food factories use dyeing for nylon, wool, silk, plastics or biological stains. More than 10.000 different dyes and pigments are known to be used in industries, and 0.7 million tons of synthetic dyes are produced annually worldwide, as reported by Saratale, et al. [**4**], an approximately 280.000 tons of textile dyes are discharged every year. 10 – 15% of the approximately 10^5 tons of dye produced globally each year are released into the environment. To minimize the negative environmental consequences of dye release, improved water remediation systems are needed. Several strategies for removing dyes from the environment have been investigated, including chemical oxidation, membrane filtration, ion exchange, and most commonly, adsorption [**5**]. Activated carbon is the primary adsorbent material employed for water purification because of its high capacity, porosity, and versatility in adsorbing different pollutants. Despite these useful properties, making and regenerating activated carbon is costly, leading researchers to explore alternative adsorbents. Attempts have therefore been made by many researchers to find inexpensive alternatives. Most research undertaken for that purpose has focused on the use of polymer based composites (hydrogel) due to their sustainable sourcing, biodegradability and low cost.

2. Hydrogel

Hydrogel can simply be described as a three-dimensional hydrophilic polymer material. It can be classified as natural, synthetic or hybrid, depending on the source of the constituting polymers. The hydrophilic groups within the structure such as hydroxyl, carboxyl, and amide that allow it swell in water and hold a large amount of water. The chemical and physical crosslinking of the individual polymer chains ensure that the hydrogel remains stable to a certain extent. This can be performed in a number of ways such as by covalent bonds (chemically), using ionizing radiation to generate main-chain free radicals which can recombine as crosslink junctions, crosslinked by non-covalent interactions as entanglements, electrostatics, and crystallite formation (physically) or by a combination of both. The cross-linked polymer network is highly sensitive to stimuli such as solvent composition, solutes, pH, temperature, electric field, and light [**6**].

Around 1900, the term 'hydrogel' first appeared in the scientific literature when it was used to describe a colloidal gel of inorganic salts [**7**]. Hydrogels as we know them today were first reported in 1960 by Wichterle & Lim [**8**], cross-linked macromolecular networks swollen

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with water. In the two decades following this discovery, hydrogel research has been focused mainly on relatively simple, chemically crosslinked synthetic polymer networks. In this period, PAM (PolyacrylAMide) is an important hydrogel-forming polymer. Although it was initially used in industrial applications such as agricultural gels, extensive researches has also been performed within this stages as potential candidates for biomedical applications especially for the physical retention of cells and enzymes. PAM gels have still keeping their importance as the basic starting polymeric material. They have recently found widespread biomedical application as soft tissue fillers, augmentation materials and adsorbent for environmental applications. Then, starting in the seventies, a different concept of hydrogels gained prominence: second-generation materials that can respond to specific stimuli, such as changes in temperature, pH, or the concentration of certain molecules in solution. These specific stimuli can be used to trigger similar specific events such as polymerization of the material, a drug delivery, or the formation of an in situ pore. Finally, third-generation hydrogels focused on the research and development of stereocomplex materials. A detail of the historical progress of the hydrogel for biomedical use can be found in the recent paper released by Buwalda, et al. [9].

2.1. Production of hydrogels

Most hydrogels are formed by polymerization of vinyl monomers containing hydrophilic groups with multifunctional vinyl monomers or by crosslinking reactive functional groups of hydrophilic polymers. Various agents are used to promote cross-linking. Temperature, UV (UltraViolet) or gamma radiation, magnetic field, electric field, pressure and sound are the main crosslinking agents for physical crosslinking while for chemical crosslinking, ionic solvents and enzymes are generally used [10 – 12]. It is assumed that chemical crosslinking is a powerful method that produces strong and mechanically stable hydrogels. By manipulating the chemistry of the hydrophilic segments in the polymers and degree of crosslinking, hydrogels may be tailored to exhibit specific properties [13]. Main components of the hydrogel synthesis process are monomer, cross linker and initiator (**Figure 1**).

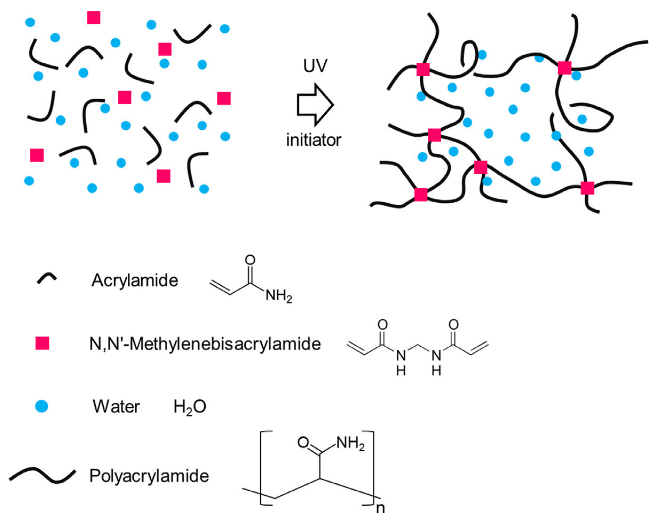

Figure 1. Synthesis of PAM hydrogel. Precursor is mixture of acrylamide as monomer, crosslinker (N'N-methylenebisacrylamide) as initiator and water [14].

Beginning with 1960, several synthesis methods has been offered in literature. According to [15], these methods may classify mainly as follow:

- Bulk polymerization (**Figure 2**) occurs by combining two or more monomers with the aid of a suitable initiator for hydrogel formation. In this polymerization, the monomers form a homogeneous hydrogel composition.
- Solution polymerization / crosslinking (**Figure 3a**) occurs by reacting ionic and neutral monomers together with the appropriate crosslinking material. The reaction is initiated with the help of UV light or using a redox initiator system.
- Suspension polymerization or reverse suspension polymerization (**Figure 3b**) occurs by dispersing the initiator as a homogeneous mixture in the hydrocarbon phase as well as the monomers.

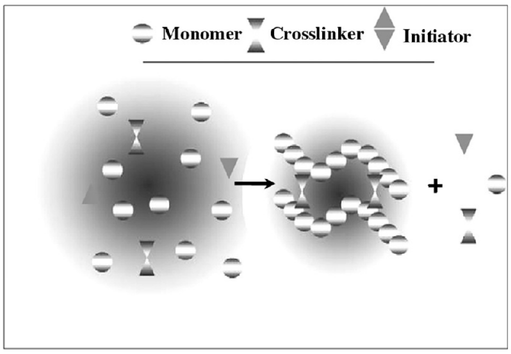

Figure 2. Bulk polymerization [15].

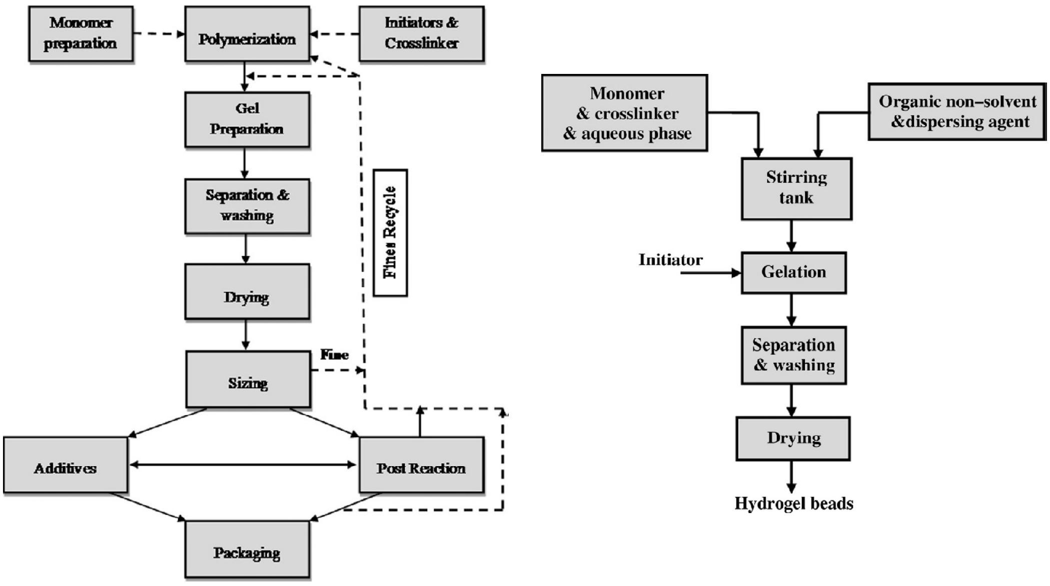

Figure 3. Schematic flowsheets of solution (a) and suspension (b) polymerizations [15].

The suspension polymerization process flow sheet of **Figure 3b** is very similar to the solution polymerization process, with the exception that water replaces the solvent and the reactor operates adiabatically. Polymerization by irradiation involves the use of high energy radiations such as electron beams / gamma rays as an initiator to prepare the hydrogel. As simply discussed above, today, hydrogels can be used in a wide range of applications from biomedical applications to environmental use.

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For these applications, although biomedical usage consists of the main part of the performed researches and applications, it's usage as adsorbent for the treatment of harmful impurities from wastewater in environmental applications is also one of the prominent research areas. The functional groups in the 3D network perform a selective and effective adsorption process by making the equivalent bond with the target molecules, the amorphous and soft structure of the hydrogel adversely affects the adsorbent stability during the process, and also requires long processing times to reach the desired adsorption capacity. Furthermore, hydrogels with chemical crosslinks need to undergo extensive purification steps to remove toxic crosslinking reagents prior to use, complicating their production [**15**]. Therefore, the new approach is the production of composite hydrogel where the synergistic effect is created by strengthening the polymeric structure with organic or inorganic additives. The presence of inorganic matter in the hydrogel composition modifies the strength properties of conventional hydrogel. Inorganic additives can be metallic nanoparticles, as well as oxides (graphene oxide) and nano-or micro-sized clay minerals such as kaolin, bentonite montmorillonite. In this context, montmorillonite and bentonite are the most preferred mineral additives due to their high adsorption capacities for organic compounds and high polymer–clay interface reactions.

2.2. Nanoparticles and fabrication of nanocomposites

Nanoparticles are of scientific interest as they act, as bridges between bulk materials and atomic or molecular structures. A bulk material has constant physical properties regardless of its size, but at the nanoscale, size-dependent properties are getting important. The interesting and unexpected properties of nanoparticles can be attributed to the large surface area, and this dominates the contributions made by the small bulk of the materials. For example, titanium dioxide impart a self-cleaning effect when it is nanosized, nanoparticles of zinc oxide have superior UV blocking properties compared to their bulk substitute is therefore they are often used in the preparation of sunscreen lotions. The usage of nanoparticles dates back to the Roman time, in the 4th c. the famous Lycurgus cup (**Figure 4**) made of dichroic glass, as well as in the 9th c. in Mesopotamia for creating a glittering effect on the surface of pots. Pottery from Middle Ages and Renaissance often retains distinct gold or copper colored metallic glitter. This luster is caused by a metallic film that was applied to the transparent surface of a glazing [**16**].

Figure 4. Famous "Lycurgus Cup" is one of earliest known uses of nanotechnology in human history [**17**].

Polymers are often reinforced with various sized fillers to overcome some of the limitations of polymers and thus expands their applications. Nowadays, composite materials represent one of the most active fields in the polymer industry. Many different types of fillers, carbon black, calcium carbonate, glass fibers and talc in the micrometer size range have been added into polymers to provide an improvement of the final product properties. However, this improvement could only be achieved at high filler concentrations, which lead to an increase in the viscosity of the material and, hence, problems in processing. In case of micrometer size, in recent years, it has been observed that the addition of just a small quantity of nano-sized layered materials greatly improved the properties of virgin polymers without affecting their processability [18].

Nanocomposite materials are multi-phase materials in which at least one of the phases is in the Nano Space. In general, nanomaterials provide reinforcing efficiency because of their high aspect ratios. The properties of a nanocomposite are greatly influenced by the size scale of its component phases and the degree of mixing between the two phases. Depending on the nature of the components used and the method of preparation, the final properties of the composite material are significantly affected. Today, nanocomposite materials are used as viable alternatives to overcome the limitations of different engineering materials. It offers completely new application opportunities to solve changing barriers in fields such as medicine, pharmaceutical industry, electronics, environmental and energy industry. Composed of metallic and polymeric materials, the nanocomposite material provides an advantage in maintaining properties such as overcoming defects. These materials represent the multiphase transition of matrix material and reinforcement material. The reinforcement material is a dispersed phase, usually organic or inorganic nano particles, glass fiber, organic fiber, etc. Fibrous materials such as, matrix material is a continuous phase and includes metallic, inorganic non-metallic and polymer matrix materials. Therefore they are classified mainly into three classes: metal matrix, ceramic matrix and polymer matrix nanocomposites [19, 20].

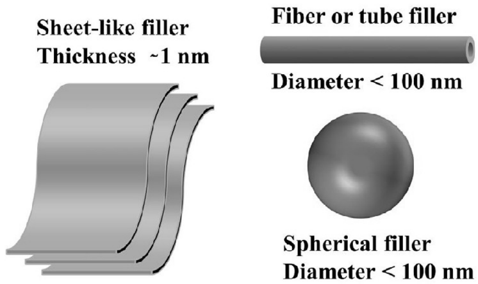

Figure 5. Schematic diagrams of three types of nanoscale fillers [21].

Depending on the dimensions and the type of the dispersed nanoscale filler or additives, polymer nanocomposites can also be categorized into three major classes (**Figure 5**). In the first class, the two dimensional (2D) nanoscale fillers such as layered silicate, graphene or MXene in the form of sheets of one to a few nanometer thick and of hundreds to thousands nanometers long are present in polymeric matrices. In the second type, two dimensions are in nanometer scale. These nanoscale fillers include nanofibers or nanotubes, e.g., carbon nanofibers and nanotubes or halloysite. The third type is the nanocomposites containing nanoscale fillers of three dimensions in the order of nanometers. These nanoscale fillers are iso-dimensional low aspect ratio nanoparticles such as spherical silica, semiconductor nanoclusters and quantum dots.

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More information on the modifying effects of various nanofillers on mechanical and physical properties of polymer nanocomposites, the three basic aspects of processing, characterization and properties were critically reviewed recently by Fu, et al. [21].

2.2.1 Nano composite hydrogel (NCH)

As briefly discussed above, basic or pristine hydrogels usually suffer from low mechanical strength and limited stiffness due to their intrinsic structural inhomogeneity and lack of effective energy dissipation mechanism. Therefore, several affords have been performed to develop a new kind of hydrogel material with high mechanical properties for practical applications in literature. Various hydrogels fabricated by different methods have been reported [22 – 25], such as double-network hydrogels (DN gels), nanocomposite hydrogels (NC gels), tetra polyethylene glycolhydrogels (tetra-PEG hydrogels), sliding-ring hydrogels, macromolecular microsphere composite hydrogels, and physical interaction hydrogels (including hydrogen bonding, dipole–dipole interaction, hydrophobic interaction, and electrostatic interaction). Within these possibilities, addition of nanomaterials with different bases is accepted as the most preferred method used to attain nanocomposite hydrogels with desired properties. Carbon-based nanomaterials (carbon nanotubes or graphene, nanodiamonds), polymeric nanoparticles (dendrimers and hyper-branched polymers), inorganic / ceramic nanoparticles (hydroxyapatite, silicates and calcium phosphate) and metal / metal oxide nanoparticles (gold, silver, graphene, iron-oxides, and graphene oxide) can be given as an examples of these nanomaterials. Among these, clay-based materials have a privileged importance due to their cost advantages, biocompatibility and widespread uses.

Historically, the term of clay can be described a material consists of small inorganic particles (part of soil fraction less than 2 mm), without any definite composition or crystallinity. Clay minerals are usually of a layered type and a fraction of hydrous, magnesium, or aluminum silicates. Every clay mineral contains two types of sheets, tetrahedral (T) and octahedral (O). Hectorite, saponite, and montmorillonite are the most commonly used smectite type layered silicates for the preparation of nanocomposites.

It was noted that the characteristic properties of hydrogels including the mechanical and thermal properties are able to be largely affected by the content of added clays [26]. These properties can be significantly enhanced when clay minerals are incorporated into the polymer matrix [20], because the increasing the clay amount will lead to an increase in the crosslink density. They revealed that these hydrogels showed very high elongation at break, close to or greater than 1500% and their tensile properties strongly depended on the content of clay. The increase of modulus and strength values is proportional to the content of clay. In addition, clays can improve the higher toughness of hydrogels based on the formation of an intercalated architecture with more cross-linking points [27]. The incorporation of clay nanoparticles into polymer matrices leads to development of more strong materials with higher glass transition temperature and mechanical properties. However, long-standing problems for polymer–clay nanocomposites include true exfoliation of clay particles in discrete layers, homogeneous distribution of clay layers throughout the polymer, and randomness of clay sequences. It is important to know that the physical mixture of polymer and layered silicate always may not form nanocomposites with desired properties. Solid layered silicates usually contain hydrated Na^+ or K^+ ions. To make layered silicates miscible with other polymer matrices, hydrophilic silicate surface mostly be converted to an organophilic surface, which can be accomplished by ion exchange reactions with cationic surfactants, e.g., $Na_x(Al^{2-}{}_xMg_x)(Si_4O_{10})(OH)_2 \cdot mH_2O$ sodium montmorillonite-type layered silicate clays are available as μm size tactoids, which consists of several hundreds of individual plate-like structures with dimensions of 1 mm: 1 mm – 1 nm. These are held together by electrostatic forces (gap in between two adjacent particles, 0.3 nm). The most difficult task is to break down the tactoids to the scale of individual particles in the dispersion process to form true nanocomposites, which has been a critical issue in current researches [**28**]. The more detail on exfoliation or intercalation especially for clay-nanocomposites can be found recent paper published by Yıldız & Kurama [**29**]. **Figure 6** shows some structures of such kind. The development of these properties is the main reason for the research on hydrogel–nanoparticle composite materials obtained with improved mechanical strength. For example, silica nanoparticle hydrogel composite materials, silica nanoparticles and modified poly ethylene glycol seen in recent studies have shown much improvement in tissue adhesive property, mechanical stiffness and bioactivity.

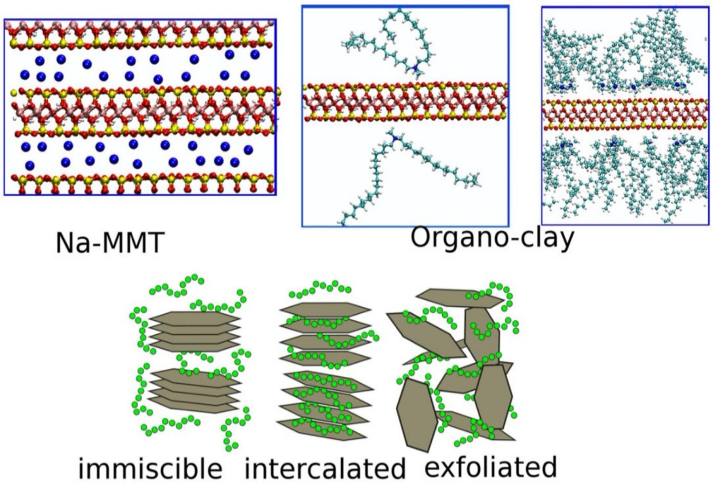

Figure 6. Atoms are colored as follows: Al = pink, Au = yellow, O = red, H = white, Na = blue, C = cyan [**30**].

Apart from clay-hydrogel composite structures a variety of functional graphene-based composites fabricated by chemical modifications or non-covalentfunctionalizes. However, the strong interaction of p–p band structure between graphene sheets makes them hydrophobic and the poor stability for direct applications. Therefore, public attention is thoroughly aroused as to the modified graphene nano-materials such as graphene oxide (GO). GO-hydrogel composite materials are also one of the interesting applications in recent years [**31 – 33**]. GO is generally accepted as one of the most preferred materials due to its hydrophilic structure, multiple functional groups and high surface area. Due to the presence of different oxygen-rich functional groups (carboxyl, carbonyl, hydroxyl, etc.), the negative potential between GO layers creates an increased effect, particularly in the adsorption of colorant molecules. A detail of preparation methods and the application areas can be found recent report released by Lu, et al. [**34**].

Consequently, although many additives are taken into consideration, clays, graphene, graphene oxide, carbon nanotubes, Fe_3O_4, chitosan, etc., due to the increased durability, adsorption capacity and reuse advantages of the additives with the individual advantages, it is seen that the vast majority of research studies are concentrated on clay-hydrogel composite or GO hydrogel composite material production.

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A wide variety of nanoparticle–hydrogel composites can be developed with the various types of nanoparticles hidden in a hydrogel. Generally, five conditions shown in **Figure 7** are used for a correct distribution.

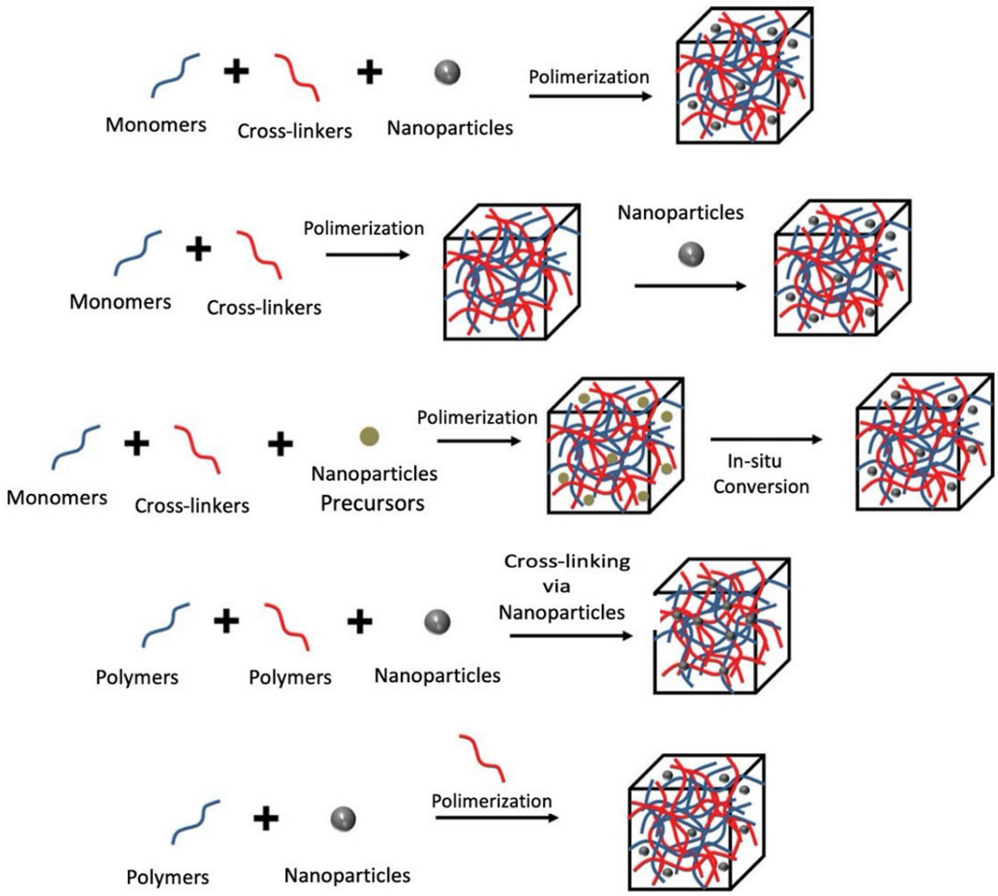

Figure 7. Five cases used to obtain hydrogel–nanoparticles [**35**].

In summary, the benefits of combining two different materials such as nanoparticles and hydrogels create advanced materials with unique properties not found in individual components, so such composite materials have become one of the areas of interest for researchers and practitioners in recent years, especially for environmental improvements.

3. Usage of composite hydrogel for environmental applications

3.1. Removal of heavy metal ions

Heavy metal ions such as Cd^{2+}, Pb^{2+}, Cu^{2+}, Mg^{2+} and Hg^{2+} from industrial wastewater constitute a major cause of pollution for ground and surface water sources. These ions are toxic to man and aquatic life as well, and should be removed from wastewater before disposal. Various treatment technologies have been reported to remediate the potential toxic elements from aqueous media, such as adsorption, precipitation, and coagulation, flotation, filtration, etc. Most of these techniques are associated with some shortcomings and challenges in terms of applicability, effectiveness and cost. However, the adsorption techniques have the capability of effectively removing heavy metals even very low concentrations and workability under different conditions and materials. Adsorption has wide pH range, high metal binding capacities, and easy operating conditions addition to its low-cost [36]. Until now, many adsorbents including nanosized materials, industrial by-products, and mineral substance have been developed and tested. Materials that qualify as effective adsorbents include inorganic particles and polymers / biopolymers. Although some nano-adsorbents have good dynamics and high adsorption capacities, using ultrafine particles for their synthesis results in difficult separation and regeneration leading to high operating costs and secondary pollution, in contrast, polymeric hydrogels exhibit a distinctive feature of water permeability and provide a rapid channel accessibility to the interior for foreign molecules. The generation of polymeric matrices in the hydrogel state reinforced with inorganic materials or mixtures of polymeric networks generating composites has been explored to improve or increase the adsorption capacity. Composite hydrogels combine effective adsorption, high specific surface area and easy applicability, so they represent a great alternative for the elimination of heavy metal ions present in aquatic ecosystems. The state of the art of materials, strategies to generate composites in a hydrogel state with properties adapted for the adsorption of heavy metal ions can found a review published by Muya, et al. [37].

For composite hydrogel, the presence of hydrophilic functional groups, such as carboxylic acid, amine, hydroxyl and sulfonic acid groups that act as complexing agent for the removal of metal ions from aqueous solutions. Interaction and sorption of organic pollutants and metal ions on to polymers chains that becomes accessible only after the hydrogel opens up in aqueous phase. The network of hydrophilic polymers can swell in water or biological fluids and hold a large amount more than 400 times its original weight more than 20% of their dry weight. Hydrogels can be regenerated as it is insoluble in water because of the presence of chemical crosslink. Adsorption of the metal ions by hydrogels takes place by the attraction mechanism, depending on the difference in charge between the positively charged metal cations and the negatively charged active sites distributed everywhere along the hydrogel structure and these active sites govern the whole uptake of the metal cations by the hydrogels. The most widely abundant function groups present in the structure of any hydrogel are hydroxyl groups and carbonyl groups. More information on the synthesis of the hydrogels for waste water treatment and insight into increase in selectivity, efficiency and reusability of hydrogels can found a review released by Shalla, et al. [38].

A recent paper that was published by Ma, et al. [39] can be given another interesting example for the hydrogel usage. In this study, an enhanced double network hydrogel adsorbent of poly(vinyl alcohol) / poly(2-acrylamido-2-methyl-1-propanesulfonic acid) or PVA / PAMPS was prepared by simple free-radical polymerization. The authors reported that the introduction of multifunctional groups (NHR, $-SO_3H$ and –OH) endowed the adsorbent with both chelating and ion exchange function. The maximum adsorption capacities of Pb^{2+} and Cd^{2+} were reported as 340 and 155.1 mg/g, respectively. The removal efficiencies reached 88.1% for Pb^{2+}, 91.4% for Cd^{2+}, 70.4% for Zn^{2+}, 77.4% for Cu^{2+}, 42.5% for Mn^{2+}, 45.1% for Ni^{2+} and 95.4% for Fe^{3+} using 2 g/L adsorbent in 2 h. Moreover, it was noted that, the adsorbent showed a good reusability, and the removal efficiencies maintained 94% for Pb^{2+} and 93% for Cd^{2+} in the fifth cycle.

The hydrogels commonly applied in water / wastewater treatment was mainly classified into three classes according to their shape included hydrogel beads, hydrogel films, and hydrogel nanocomposites. Recently, Tran, et al. [40] published a review based on several research papers on the removal of pollutants such as hydrogels and heavy metal ions, dyes and radionuclides from water / wastewater to elucidate reactions between pollutants and the potential for recycling and regeneration In this study, protein-based hydrogels, GO, itaconic acid (IA), 2-hydroxyethyl acrylate (HEA), combination of IA with 2-hydroxyethyl acrylate, pH-sensitive, sodium alginate / itaconic (NaAlg/IA) hydrogels, clay based hydrogels and the hydrogels prepared by based on combining CS, AA, and organically modified nanosilica by 3-aminopropyl triethoxysilane (APTS) for removal of heavy metal ions has been reviewed. The information on adsorption kinetics and mechanisms of adsorbents on hydrogel was also given.

3.2. Textile industry effluents and remediation

Dyeing in various manufacturing processes such as textiles, leather, rubber, paper, plastics, pharmaceuticals and food is among the most polluting industrial activities as it generates enormous amounts of colored wastewater [41]. More than 10.000 different dyes and pigments are known to be used in industries, and almost 0.8 million tons of synthetic dyes are produced worldwide annually. About 10 – 15% of synthetic dyes are lost during different processes of textile industry. Manufacture and use of synthetic dyes for fabric dyeing has therefore become a massive industry. Synthetic dyes have provided a wide range of colorfast, bright hues. However, their toxic nature has become a cause of grave concern to environmentalists. Use of synthetic dyes has an adverse effect on all forms of life. Presence of sulphur, naphthalol, vat dyes, nitrates, acetic acid, soaps, enzymes chromium compounds, and heavy metals like copper, arsenic, lead, cadmium, mercury, nickel, and cobalt and certain auxiliary chemicals all collectively make the textile effluent highly toxic. These organic materials react with many disinfectants, especially chlorine, and form byproducts (DBPs) that are often carcinogenic and therefore undesirable. This effluent, if allowed to flow in the fields, clogs the pores of the soil resulting in loss of soil productivity [42].

According to a Business Research Company's research report, major driving factors of the synthetic dyes and pigments market are increasing demand for high-performance pigments (HPP), and growing opportunities for new applications in end-user industries such as printing inks, textile, construction and plastics. The global paper, plastics, rubber, wood and textile market is estimated to grow from $5,782.5 billion in 2020 to $8,049.7 billion in 2025 at a compound annual growth rate (CAGR) of 6.8%, implying the demand of synthetic dyes in the market. This situation is remarkable in terms of showing the size of the increasing threat with the increasing use of paint.

Textile effluents are usually treated by physical, chemical processes or biological remediation such as sorption, oxidation, flocculation, etc. Color removal by activated carbon, H_2O_2, sodium hypochlorite and other chemical agents has been widely practiced in the textile industries [42]. Although activated carbon remains the most widely used adsorbent, its relatively high cost restricts its use. Many recent studies focus on the development of clay based adsorbents as the most promising cost-effective new alternative material. The use of montmorillonite (MMT) and its modified forms for pollution control has been reported by Wibulswas [43]. In this study, montmorillonite and its derivatives were examined as an alternative sorbent for methylene blue adsorption as batch and fixed bed forms. The modified clays were prepared by altering the surface properties of the raw montmorillonite clay, from organophobic to organophilic, with four types of quaternary ammonium compounds namely, tetramethylammonium chloride (TMA), tetradecyltrimethylammonium bromide (TDMA), hexadecyltrimethylammonium bromide (HDTMA, and benzyldimethylhexadecylammonium chloride (BDHDMA). It was reported that the modification of MMT by surfactant positively affects the exfoliation of clay layer and TMA-clays have the higher BET (Brunauer–Emmett–Teller) surface area than those of the raw clays and the organic clays. The adsorption capacity of MMT was calculated as 322.6 mg/g or 100 meg/100 g of clay).

In many subsequent studies, clay-based hydrogels have been reported as effective alternative adsorbents for dye removal [**44 – 47**]. Li, et al. [**48**] proposed that use of nanoclay for the synthesis of nanocomposite (NC) hydrogel in their study. NC was prepared by incorporating the nanoclay (laponite (Lap) XLS) into a poly(acrylamide) (PAAm) hydrogel by the in situ polymerization method without any organic cross-linker. It was reported that the adsorption of crystal violet (CV) dye by the hydrogel increases as the concentration of the dye increases. The cationic dye adsorption ability of the NC hydrogel increased with increasing clay content in the NC hydrogel. Such a binding was found to be responsible for the very large amount of monovalent organic cations adsorbed to laponite, which attained its cation exchange capacity. In Lap XLS, negative sites occur at the external surface, and may form a complex by the interaction between one dye cation and one of these negative sites of clay. Therefore, electrostatic interactions between the dye molecules and hydrogels are dominant.

Except than well-known surfactants, the use of cationic surfactant (CTAB) and anionic surfactant (SDS) for the modification of Ca–montmorillonite (Ca–MMT) has been also reported by Zhang, et al. [**49**]. The authors reported that MMT–CTAB–SDS exhibited excellent dispersion property and the plates with few silicate layers can be observed. In this study, Ca–MMT was modified with CTAB and then expanded by SDS with the synergistic effect. The usability of cationic surfactant (Hexadecyltrimenthylammonium chloride) modified bentonite clay as an efficient adsorbent for the removal of basic dyes such as methylene blue (MB), crystal violet and rho-damine B (RB) from aqueous phase was also given as an interesting example. In this study, it was noted that organomodified clay has a better capacity for the removal of three dyes. The maximum dye sorption efficiencies were calculated as 99.99% for MB, 95.0% for CV and 83.0% for RB at a pH of 9.0. The adsorption capacity for the dyes was found to be 399.74, 365.11 and 324.36 μmol/g for MB, CV and RB, respectively, at 30°C.

Another interesting study for the surface modification of clays was reported by Olusegun, et al. [**50**]. In this study the pretreatment of clay by spray drying before adsorption was tested. The adsorption tests were carried out using methylene blue and results showed that the adsorption capacity was influenced by solution pH, with maximum adsorption at pH 10 and 120 min contact time. Adsorption kinetics data were well fitted to pseudo-second order kinetics model. It was stated that spray dried method can also be concerning for pretreatment. It was proposed that modified clay has a better performance than the chemically modified and raw clay with adsorption capacity of 168 mg/g (at 333 K).

More recently, dyes adsorption using clay and modified clay has been well reviewed a by Kausar, et al. [**51**]. In this report, appropriate conditions for clay-dye system and adsorption capacities of a variety of clays were presented and sorption process was critically analyzed. As a conclusion the authors reported that clays (natural and modified) are affective adsorbents for the purification of wastewater containing dyes.

Instead of clay and GO-based hydrogels as an alternative adsorbent, cellulose-based hydrogels (CBHs) can also be given interesting example as innovative materials that have been extensively studied in recent years due to their high abundance, biodegradability, non-toxicity and excellent adsorption capacity. The most recent review, reported by Akter, et al. [**52**],

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highlights different CBH adsorbents in the context of removing dyes and heavy metals from wastewater following various synthesis techniques and adsorption mechanisms. This study also outlines the various process parameters required to optimize the adsorption capacity, followed by future research directions. MB, crystal violet, cross-linking for Cu^{2+} treatment, instant gelation, graft polymerization, freeze / thaw, etc. Electrostatic interactions, ion exchange and H bonding was reported as main mechanisms for the cellulose based composite hydrogels prepared by crosslinking, instantaneous gelation, graft polymerization, freezing / thawing and so on, for the treatment of MB, crystal violet, $Cu^{2+,}$ Pb^{2+}, Ni^{2+}, Zn^{2+} and Cd^{2+} ions.

4. Conclusion

With the rapid development of nanotechnology in the past few years, the study on the nanocomposites has been increasingly become important in the development of new materials for advanced applications. To fulfill the growing needs of multifunctional materials, nanocomposites are the right choice as these are not only the versatile class of materials, but also have a high level of integrated association. It is a multidisciplinary field which includes the knowledge of scientific background as well as technological aspects to create macroscopic engineered materials obtained through nano level structures. These materials are suitable materials to meet the emerging demands arising from scientific and technologic advances. Outstanding potentials of nanocomposites can be exemplified by the massive investments from many companies throughout the world. The important aspects for nanocomposite especially form of hydrogel, is that it provides plausible benefit to many of our industrial sector like electronics and electrical industry, chemical industry, transportation sectors, health care organizations, and above an all the protection of the environment. Hence, these are expected to have high impact on making the environment cleaner, greener, and safer in the coming years.

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