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Hydrogels for Wastewater Treatment: A Review

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Abstract: ***The requirement of fresh drinking water increases day by day rapidly, because of industrialization the rising the industrial discharge which passed directly into the river which caused enhanced the contaminated water in water reservoir. The deficiency of pure water can be maintained by the purification of river and other reservoir. There are going to search effective, sustainable and economical technologies that applicable for the treatment of water. The hydrogel polymeric materials that have three-dimensional hydrophilic structure and also amazing swelling capacity that developed as capable substance shows waste water treatment. Due to the availability of flexibility structural behavior, wide surface area and versatility in functional group enhanced adsorption and elimination of toxic metals, organic dyes, pharmaceuticals and other evolving contaminants. For this purpose, various natural and artificial polymeric hydrogels, hydrogels with nanocomposite have been industrialized to facilitate adsorption capacity, selectivity towards pollutants and revival capacities. This review illustrates the ethics of polymeric hydrogel for wastewater treatment, pollutant removal process, current developments, limitations, forthcoming perceptions, developing hydrogel with modern treatment technologies.***

Keywords: Waste water, Polymeric hydrogel, nanocomposite, pollutants, swelling capacity

1. Introduction

The waste water is produced by the contagion produced by industrial activity that directly into the river without treatment, domestic and other sources of contaminated water also discharged directly into the water reservoir like Lake, River etc. [1]. Pollutants like organic dyes, heavy metals, pesticides and other pollutant that caused adverse effects to environment and health on living being [2]. There are various methods like, coagulation, flocculation [3], ion exchange [4]and activated carbon adsorption [5], [6] are applied in waste water treatment but these processes have some limitations as limited efficiency, production secondary pollutants and no economic value. Due to the unavoidable problem, hydrogels which have specific physicochemical properties it attracts the attention of researcher towards substitute materials for waste water treatments that minimize the above produced problem. Hydrogels are polymeric substances that formed by the cross-linking process to some other monomers [7]. Which have large amount of water absorption capacity and it also maintained their structural reliability. Hydrogels have three-dimensional arrangement which bring of the functional groups like –OH, –COOH, –NH_2, and –SO_3H, generate active sites for holding and removal of pollutants [8]-[9].

Chitosan [10], cellulose [11], alginate [12], starch carrageenan [13], naturally occurring polymeric hydrogels that have biologically degradable and also shows eco-friendly nature, but polyacrylamide [9], polyacrylic acid [8] and polyvinyl alcohol [14] are synthetic polymers it enhanced stability in their structure and flexibility. Currently advancement in hydrogels nanocomposite again improved the activity likes much absorption, selectivity and reusability through assimilating of nanoparticles, carbon substances, and clay. This review précises the character of hydrogels in wastewater treatment, directing on pollutant removal processes, current applications, challenges, and future directions.

2. Classification of Hydrogels in Wastewater Treatment

The hydrogel which are frequently used in the wastewater treatment which are illustrated in figure1. These hydrogels are mainly classified into three categories-[15]

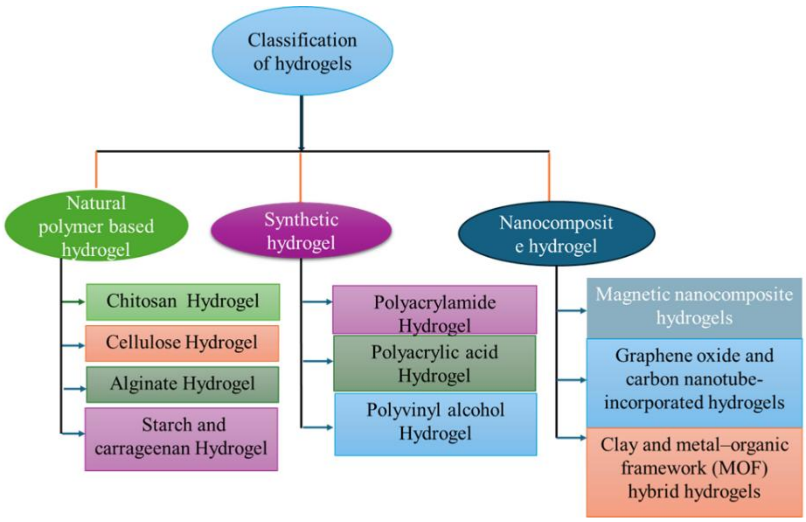


Figure 1: Classification of hydrogels

2.1 Natural Polymer-Based Hydrogels

2.1.1 Chitosan hydrogels

The hydrogels with chitosan are capable toward the microbial degradability substances which have much potentials to purifications of water. It removed a variety of pollutants likes heavy and hazardous metals, organic dyes, pollutants from pharmaceuticals and bacteria. The skeleton of chitosan contains a number of functional groups of hydroxyl and amino groups which facilitate the interaction with pollutants present into the water and also capable to adsorption towards pollutants. After that pollutants can easily remove from water. These hydrogels effectively show adsorption with heavy metals like Pb^{2+}, Cr^{6+} and Cd^{2+} etc. are given in figure 2.[10] [16]

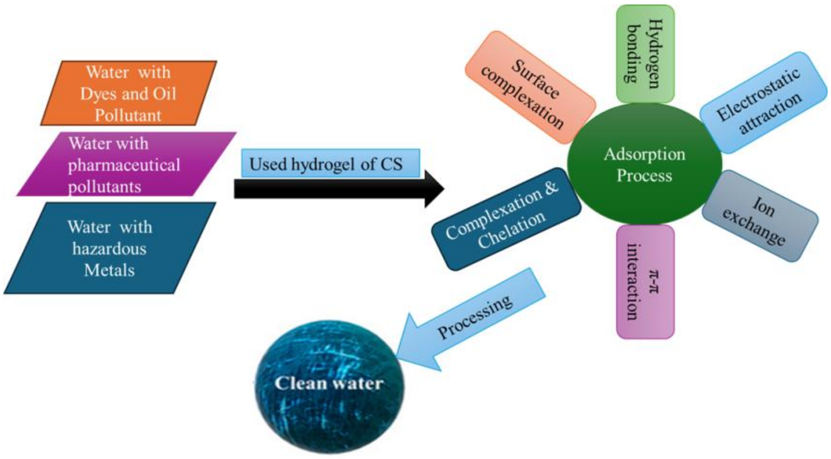


Figure 2: Chitosan based hydrogel and their applications

2.1.2. Cellulose hydrogels:

The skeleton of cellulose contains rich of hydroxyl (-OH) functional groups and acetal groups which produced β-1,4 glycosidic linkages with anhydro glucose units. The availability of hydroxyl groups facilitates hydrogen bonding that provide strength to the cellulose and linkage of acetal linkage which are maintained the backbone of polymer. [11][17]

The structural components of cellulose are helpful for the pollutants viz hazardous metals, dyes and other organic toxins present in polluted water. Due to their more water absorption capacity, porous structure and availability of functional enhanced the adsorption potential of polymer. This polymer is easily degradable in environment, non-toxicity substances and it provide economical to use as conventional process. This polymer used adsorption, filtration and membrane separation process in wastewater treatments. This polymer can be easily modified, by the modification enhanced their efficiency and facilitate capability selectivity to holding to pollutants, given in figure 3.

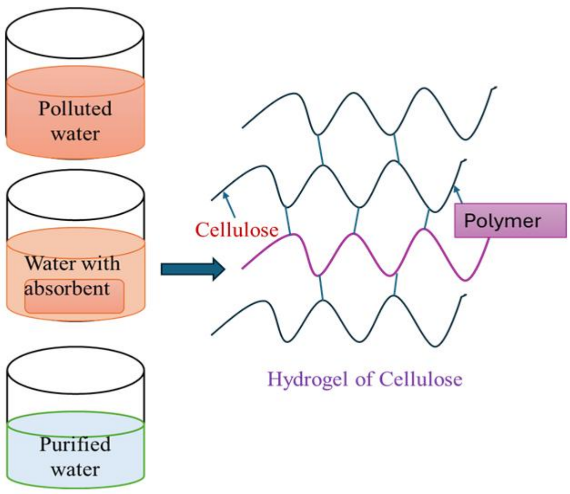


Figure 3: Cellulose based hydrogels and application in wastewater treatment

2.1.3 Alginate hydrogels:

Alginate a natural polymeric hydrogel also used in wastewater treatment, it behaves as active, justifiable adsorbents that helped into the removal of toxic metals, dyes form polluted water basically cationic pollutants. Alginate obtained from naturally occurring polysaccharides, economically valuable, ecofriendly and easily degradable with environmental microbes. The presence of hydroxyl and carboxyl function groups enhanced adsorption by the involved ion exchange and chelation process. Natural polymeric materials have low mechanical strength durability, it also modified with other chemicals form grafted compounds easily, which boosted activity and stability towards various applications. [12]

2.1.4. Starch and carrageenan hydrogels:

These class of hydrogels are naturally occurring polymers; it frequently applied if treatment of polluted water and have biodegradable and ecofriendly in nature. It can be easily modified and tailored with other chemicals formed composites that shows as flocculants and adsorbents for removal of dyes, toxic metal and suspended solids, which are as-[13]

2.1.4.1. Used of starch in Wastewater Treatments

Inherent starch polymeric materials have small surface area and sprangly soluble in water while their functional groups tailored with other chemical groups it potentially removed a number of pollutants. It involved some common mechanisms.

2.1.4.1.1. Flocculation-

The figure 4 expressed the coagulant that acts as bridged in between the pollutant's particles present in water and long chain of polysaccharides helped in adsorption to colloidal particles of pollutants which favored them to come closer to each other and form huge, dense floc that easily settled down and removed easily from water.[3]

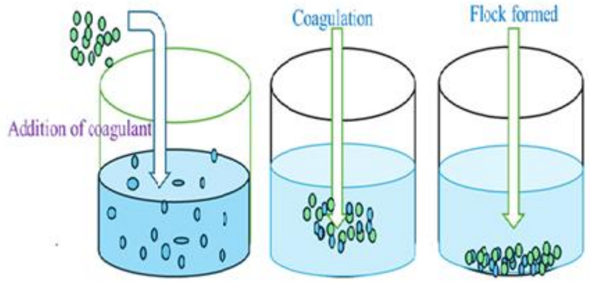


Figure 4. Flocculation mechanism of hydrogel

2.1.4.1.2. Adsorption

Hydrogel with tailored starch is an active adsorbent to heavy, toxic metals such as lead (Pb^{2+}), copper (Cu^{2+}) and nickel (Ni^{2+}) etc. and organic contaminants e.g. carboxymethyl sago starch, citric acid hydrogel are used for removal of above pollutants given in figure 5. [5] [18]

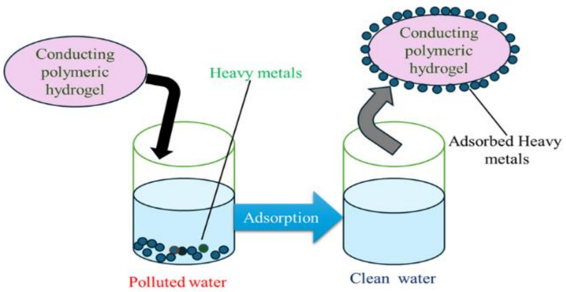


Figure 5. Adsorption mechanism of hydrogels

2.1.4.2. Used of carrageenan in Wastewater Treatments

These hydrogels a polysaccharide which are obtained from natural seaweed and have no toxicity, easily degradable substances. There are sulphates functional groups are present in their structure which make to favorable for treatment of polluted water.

2.1.4.3 General mechanism applied in treatment of water

2.1.4.3.1. Adsorption and Flocculation

Polymeric hydrogel with carrageenan facilitates both mechanism for removal of toxic metals, dyes, bio-waste compounds. Electrostatic and hydrogen bonding phenomenon developed in the removal of above pollutants present in water. [3][18]

2.1.4.3.2. Membrane filtration process

Development of low cost and eco-friendly membrane by carrageenan-based hydrogel which given in figure 6 that applied in filtration of water. A membrane of starch-carrageenan shows better performance in few applications as compare to Nafion a membrane which are commercially used [19].

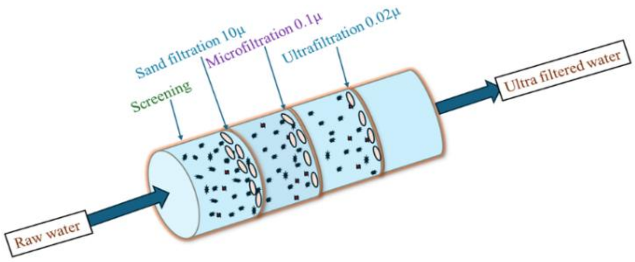


Figure 6. Membrane filtration techniques

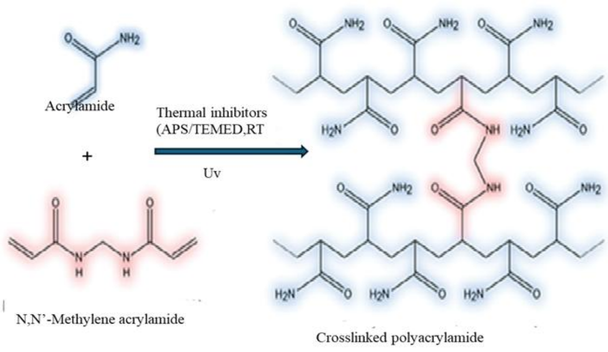
2.1.4.4. Application of collective starch and carrageenan

Collective form of the starch and carrageenan improved the exclusive character of both natural polymers to produced development environmental valuable materials that used in wastewater treatments. K-carrageenan and potato starch natural hydrogels are shows effective removal of methylene blue dye while starch obtained from potato boost up adsorption capability by hydrogen bonding and electrostatic interactions. It also improved the reusability.

3.Synthetic Polymer Hydrogels

3.1. Polyacrylamide

This hydrogel synthesized via free radical polymerization using acrylamide monomer and ammonium persulfate initiator structure of polyacrylamide and their synthesis route is shown in scheme 1. It contains $-CONH_2$ functional groups into their structure. The availability of amide groups makes favorable towards the treatment of polluted water. It involved adsorption and flocculation mechanism during the removal of pollutants from contaminated water. Researchers developed composite materials with assimilating of graphene oxide, chitosan and zinc oxide, which accelerate capability towards removal of contaminants like hazardous mental, dyes and contaminants generate by biological waste, and these materials have more reusability and improved the water quality.[9]



Scheme1. Synthetic routs of crosslinked polyacrylamide

3.2. Polyacrylic acid hydrogels

The polyacrylic acid generally it forms polyacrylate and ionic polymeric materials were prepared by polymerization process with the help of acrylic acid monomer and suitable initiators. Because of the high-water absorption capability of polyacrylic acid and selectivity towards bonding contaminants, it commonly applied in treatment of contaminated water. The efficiency of polyacrylic acid toward above phenomenon produced in the availability a number of carboxylic groups in their polymeric skeleton. These groups permit the removal of a various pollutant especially cationic toxic metals like Cd^{2+}, Pb^{2+}, Ni^{2+}, Cu^{2+} etc. and organic dyes.[8]

3.3. Polyvinyl alcohol (PVA) hydrogels:

These hydrogels which are shown in figure 7, that frequently employed in treatment of polluted water it restrained the microorganism that produced by the decomposition of organic waste materials, it also as a better adsorbent towards removal of dyes, toxic metals. The structure of PVA shows porous in nature that have better water absorbents, its structure offered appropriate atmosphere to existence of microbes and enhanced the interaction of pollutants. It has some limitation in their mechanical stability, which can be strengthening through nanoparticles or some other polymeric materials. There polymeric hydrogels easy to degrade in atmosphere, no caused adverse effect to the environment that introduced as a favorable material which used into the various process in treatment of polluted water.[14]

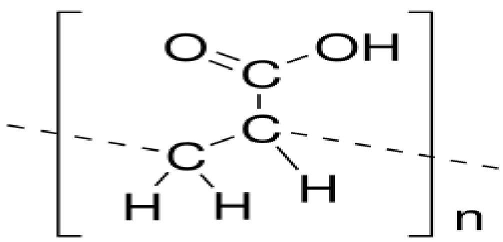


Figure 7. structure of polyvinyl alcohol

4.Nanocomposite Hydrogels

Nanocomposite base hydrogels are emerging materials that employed for the treatment of contaminated water. Such types of hydrogels have vided surface area and spongy structure that helped in admirable adsorption and photolytic abilities. Some nano particles introduced into the moiety of hydrogel for the improvement of their structural strength, durability, and functionality that provide to effective adsorbents and photocatalyst for clean water [20]. Some nanocomposites are as.

4.1. Magnetic nanocomposite hydrogels

These composite hydrogels are modern adsorbents represented in figure 8, that frequently used in treatment of polluted water. Their much porosity, huge surface area proved capability to binding with pollutants as hazardous metals and dyes. Such types of composites developed by the introducing of magnetic nanoparticles (MNPs) into polymeric hydrogel moiety to formed hybrid materials the improved mechanical strength and easily separate by using externa magnetic field fort this purpose we can used alginate, cellulose or chitosan. These composites show friendly behavior towards environment, effective to removal of contaminants and giving an adaptable and competent solution to purification of water [21].

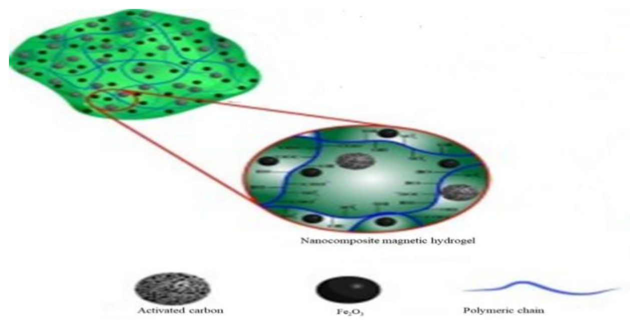


Figure 8. Magnetic nanocomposite hydrogel

4.2. Hydrogels with graphene oxide and carbon nanotube

This type of hydrogel is an advance composite material which can be synthesized by incorporating of graphene oxide (GO) and carbon nanotube within hydrogel matrix that materials frequently used in wastewater treatments, the synthetic scheme is given in figure 9. These composite materials have wide surface area and its surface can be easily modified the chemistry of GO and CNTs through absorption of water, 3D structural network of hydrogels that produced an adsorbent having very much efficiency for the removal of a variety of organic and inorganic pollutants present waste water [22]

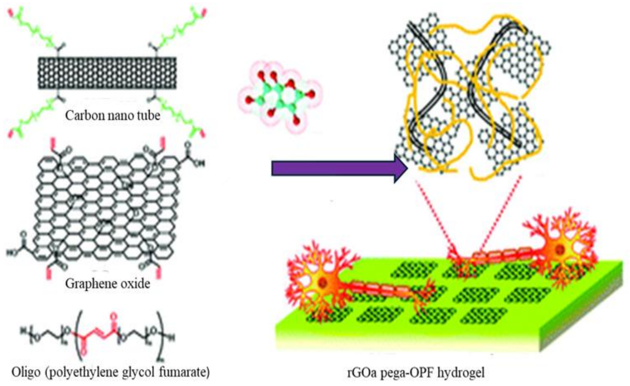


Figure 9. Graphene oxide and carbon nanotube hydrogel.

4.3. Clay and metal–organic framework (MOF) hybrid hydrogels

Hybrid hydrogel of a clay and metal organic framework (MOF) is a composite substance which provide spongy structure of MOFs by clay-built hydrogel moiety. These materials improved their characters that of their individuals' components, attached with more spongy and functional flexibility of MOFs that enhanced the durability, biologically computable clay hydrogel. These co-operative characters provide the auspicious uses in drugs delivery, ecofriendly and wounds healing [23],

5.Mechanisms of Pollutant Removal

Polymeric hydrogels in wastewater treatment involved and operate through various mechanisms as

5.1. Ion exchange

Ion exchange mechanism used in treated of contaminated water by using resin in beads form that eliminate the undesirable ions dissolved in water through swapping, shown in figure10. In this mechanism polluted water continuous passed through the resin bed, the contaminates capture by this bed. After that redeveloped resin bed by suitable chemical solution that again reestablished the effectiveness. By applying this mechanism, we can removed toxic heavy metal, salts and ammonia, particularly in the progressive refining phases of treatment and generates a good quality seepage [4].

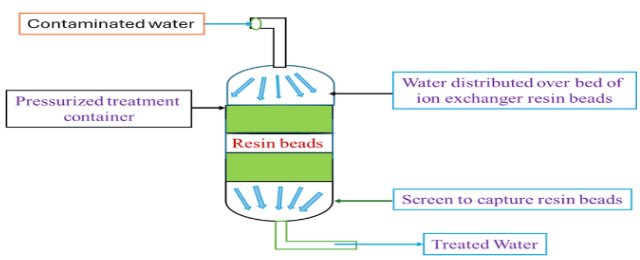


Figure 10. Ion exchange process

5.2. Electrostatic interaction

This mechanism is more important part in a various process of waste water treatments it involved in neutralization or apply charge available the surface in form of suspended or dissolved form of contaminants that allow to removal. In this mechanism coagulation, adsorption, membrane filtration and electrocoagulation process are used for removal of pollutants form wastewater given in figure 11 [24].

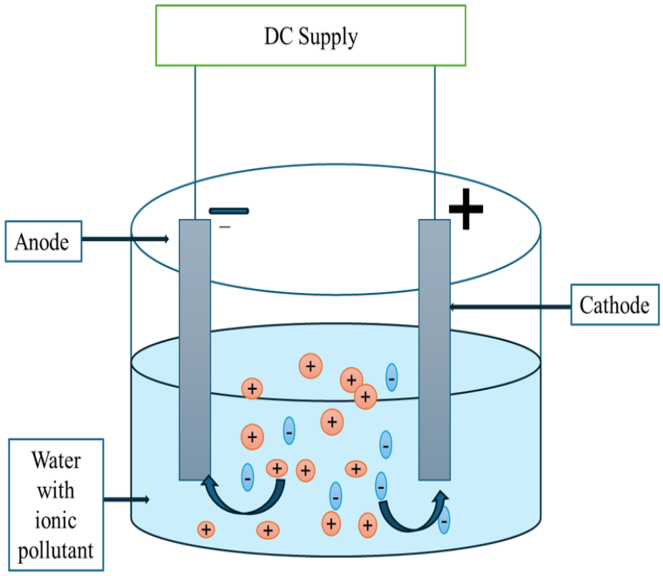


Figure 11. Electrostatic interaction in wastewater treatments

The chemical reaction carried out in electrocoagulation are-

The electro dissolution at anode as in equation 1.

$$M_{(s)} \rightarrow M^{n+}_{(aq)} + ne^- \quad (1)$$

At a time, another reaction as hydrolysis is occurred at cathode and bubbles of hydrogen are evolved as equation 2.

$$2H_2O\ (l) + 2e\ \rightarrow H_2(g) + 2OH^-_{(aq)} \quad (2)$$

There is oxygen gas release at anode reaction shown as represented in equation 3

$$2H_2O(l)\ \rightarrow O_2(g) + 4H^+(aq) + 4e^- \quad (3)$$

The metal ions available into the water passed in the solution and become hydrolysed form metal hydroxide that act as coagulants shown in equation 4.

$$M^{n+}(aq) + mH_2O \leftrightarrow M(OH)_n + mH^+ \quad (4)$$

5.3. Hydrogen bonding

This bonding is the essential intermolecular force influence the various significant route in the treatment of polluted water especially in coagulation, adsorption and membrane filtrations. In this mechanism proceed by the electrostatic attraction of hydrogen atoms with highly electronegative atoms as oxygen, nitrogen and oxygen present in contaminated molecule. The coagulation and flocculation and hydrogen bonding enhanced the accumulate small particles in the bigger form as flocs which can be eliminate form water through alluviation of flotation shown in figure 12. [25]

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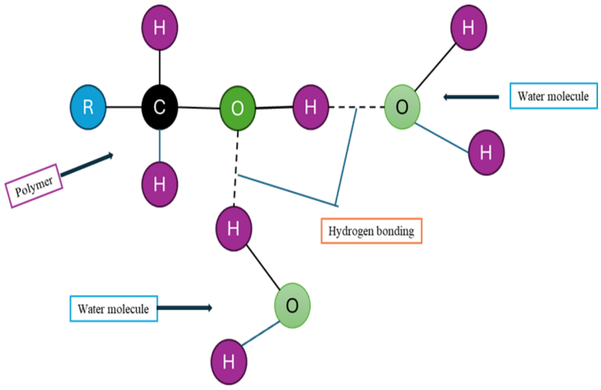

Figure12. Hydrogen bonding of polymer with water

5.4. Complexation and chelation

There is another technique which are applied for removal of pollutants from contaminated water that is a chemical method and known as complexation chelation structure is given in figure 12. By using these techniques, we can easily eliminate toxic metals viz lead, mercury, cadmium, nickel, copper, cobalt etc. this phenomenon is helped in the bonding of metal ions with suitable hydrogel formed steady complex that shows lesser toxicity and get easily eliminate from contaminated water [26].

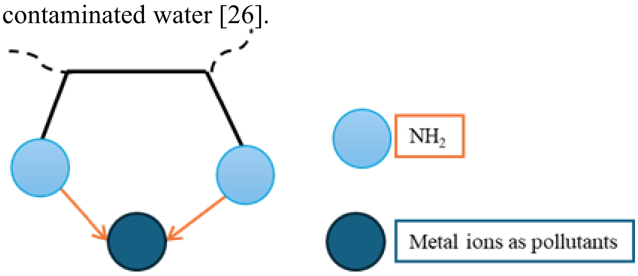

Figure 12. Complexation of metal ions with polymer

5.5. π–π stacking

It is an attractive force in between aromatic ring which are non-covalently bonding that is used in waste water treatment. It can easily remove the organic contaminants by applying adsorption process. This technique is particularly premeditated nanomaterials and adsorbent with biochar which show more affinity towards aromatic pollutants such as dyes, pharmaceuticals and polycyclic aromatic hydrocarbon. In this mechanism the force generated through the interaction of delocalized π electrons in between the ring of adsorbents substance and pollutant's molecules ring shown in figure 13. [27]

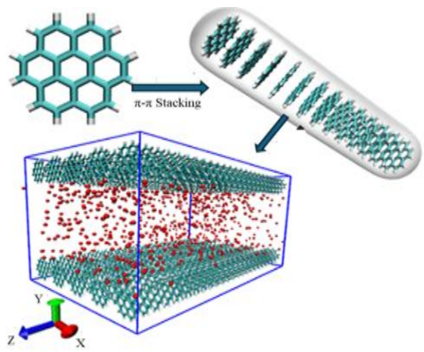

Figure 13. π–π stacking of polymer

6.Recent Applications

The chitosan–graphene oxide based polymeric hydrogels are applied in removal of heavy metal or toxic metal such as Pb^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+} etc. from contaminate water.

Hybrid hydrogels with alginate–clay having much affinity towards dyes methylene blue and crystal violet, these hydrogels removed such dyes from contaminated water trough adsorption process.

A number of hydrogels with polyvinyl alcohol used in the removal of pharmaceutical wastewater and it also applied in adsorption antibiotics and endocrine disruptors.

The magnetic based hydrogel used in the treatment of industrial effluents; it quickly separates and recycle the wastewater of textile industry.

7.Future Perspectives

The synthesis of multifunctional hybrid base hydrogel that provide the efficiency towards the removal of mixed pollutants simultaneously.

- The enhancement of membrane technology, photocatalysis and progressive oxidation system to shows harmonious effects.
- To development of cost effective eco-friendly raw substances that have multiple applications.
- To development of hydrogel having perceptive nature towards stimuli as pH, temperature and light, that provide the precise discharge and regeneration.

8.Conclusion

Hydrogels represent an adaptable and auspicious stage for treatment of wastewater because of it's their eminent adsorption capability, tunability in structure, and compatible with environment. Current improvements in usual, artificial and hydrogel with nanocomposites revealed substantial probable in dyes eliminating, heavy metals and pharmaceuticals from polluted water. Though, more study is required that minimize the limitations in stability, renaissance, and commercially production. Imminent incorporation of hydrogel systems with other cutting-edge treatment technologies may afford supportable resolutions for global water purification challenges.

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