Starch-Based Polymer Materials as Adsorbents for Water Treatment

Subjects: Engineering, Chemical

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Owing to its non-toxicity, biodegradability, and biocompatibility, starch is a naturally occurring polysaccharide that scientists are looking into as a possible environmentally friendly material for sustainable water remediation. Starch could exhibit significant adsorption capabilities towards pollutants with the substitution of amide, amino, carboxyl, and other functional groups for hydroxyl groups. Starch derivatives may effectively remove contaminants such as oil, organic solvents, pesticides, heavy metals, dyes, and pharmaceutical pollutants by employing adsorption techniques at a rate greater than 90%. The maximal adsorption capacities of starch-based adsorbents for oil and organic solvents, pesticides, heavy metal ions, dyes, and pharmaceuticals are 13,000, 66, 2000, 25,000, and 782 mg/g, respectively.

starch adsorbent wastewater treatment heavy metals dye oil organic solvents pesticides pharmaceutical pollutants

1. Introduction

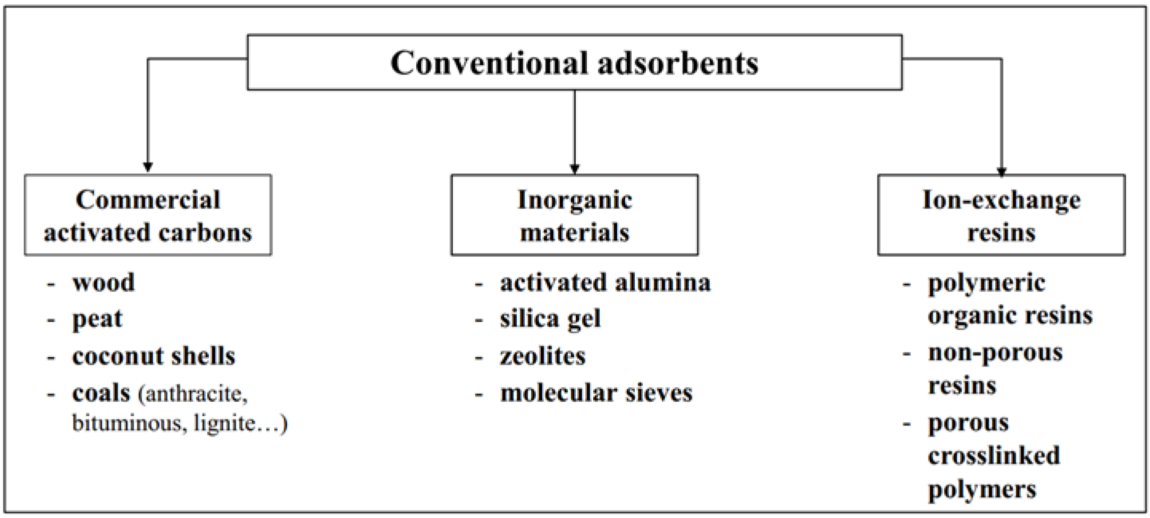
Starch is a carbohydrate and a natural component of most plants, is commercially derived from grains and serves as an important raw material in various industries such as medicine, food, chemicals, etc. Starch has been extensively studied for its potential in wastewater treatment [1][2], it is a relatively good option for wastewater treatment due to its chemical structure, biocompatibility, and biodegradability which can enhance its utilization as green adsorbent. Cassava starch, rice starch, corn starch, and potato starch are documented botanical sources of starch [3]. Starch molecules exist in two structural forms: amylose and amylopectin. Amylopectin contains a higher glucose content compared to amylose [4]. In its natural state, amylose accounts for about 20–30% of starch and amylopectin accounts for 70–80%. Starch is primarily synthesized in the chloroplast of plant leaves or the amyloplast of plant storage organs and contains lipids as well as phosphate groups [5]. However, native starch has considerable limitations when used in wastewater treatment. These limitations include low surface area, limited thermal stability, low water solubility, low molecular weight, quick degradability in water, and a lack of reactive functional groups [6][7]. To overcome these limitations and enhance its adsorption capabilities for wastewater treatment, researchers have explored various modifications of starch. Researchers discovered that incorporating a chemical functional group into the starch backbone improves the adsorption efficacy of modified starch to a variety of pollutants [6][7][8]. Several starch modifications, including starch-based grafts, polymer nanocomposites, nanofibers, nanoparticles, activated carbon, biochar, hydrogels, aerogels, and beads, have been developed to overcome these limitations [6]. Through modification and functionalization approaches, ongoing research aims to improve the adsorption capacity and selectivity of starch-based adsorbents.

2. Adsorption

2.1. Adsorbents

Adsorbents are the materials that can perform adsorption itself. These materials come in the form of porous solids with a large surface area [9]. Adsorbent selection is critical to the success of any adsorption-based water treatment process. The criteria that need to be considered to choose a material for an adsorbent is from its cost-effectiveness, availability, sustainability, suitable mechanical properties, does not disintegrate in solution, longevity, regeneration, etc. As to its performance, an adsorbent's performance is dependent on the physical structure, activation conditions, influence of process variables, solution conditions, and the chemistry of its pollutants [10].

There are five different categories that can distinguish one adsorbent from another. These categories are natural materials, manufactured materials, modified natural materials, agricultural solid wastes and industrial by-products, and bio-sorbents. These then can be divided again into two different, much more simplified groups. Conventional adsorbents and non-conventional adsorbents. Conventional adsorbents include activated carbons, such as wood, peat, coals, coconut shells; inorganic materials, such as silica gel, natural zeolites, activated alumina, and molecular sieves, which are synthetic zeolites; and ion-exchange resins, such as polymeric organic resin, non-porous resins, and porous cross-linked polymers. As for non-conventional adsorbents, these include activated carbons from solid wastes; bio-sorbents, such as chitosan, cellulose, starch, and biomass; industrial by-products; agricultural wastes; natural materials such as clays, siliceous materials, and inorganic materials; and some miscellaneous adsorbents such as cotton waste, hydrogels, etc. [11][12]. **Figure 1** presents the examples of conventional adsorbents and non-conventional adsorbents for removal of pollutants from wastewaters.



(a)

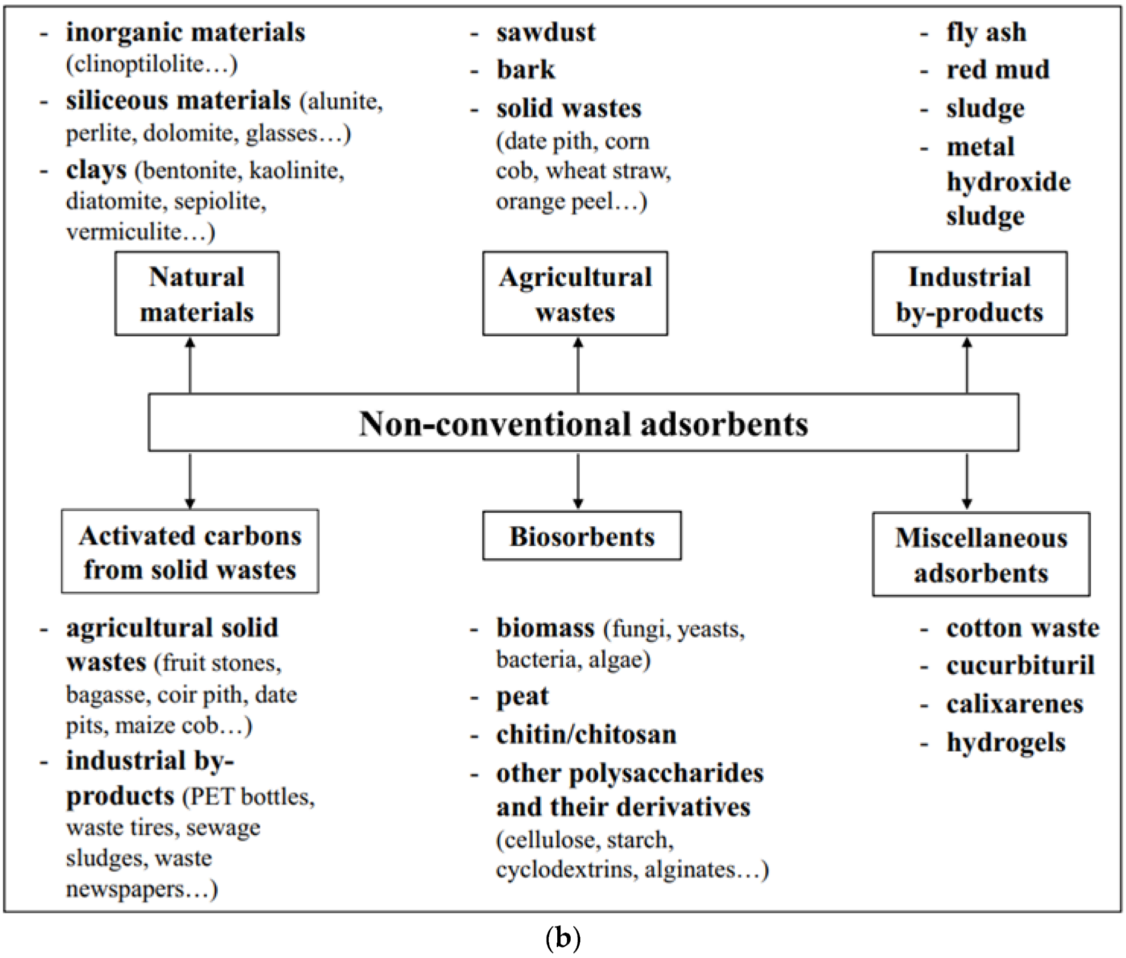


Figure 1. (**a**) Conventional adsorbents and (**b**) non-conventional adsorbents for removal of pollutants from wastewaters [13].

2.2. Starch-Based Adsorbents

Starch, the most abundant available biopolymer in the biosphere, is a homopolysaccharide with linear and branched units derived from a variety of sources, including tuber waste [14][15][16][17]. It is extensively utilized in the food industry as a source of energy in human diets, and it has discovered usages as a raw material in non-food industries for instance water treatment [18]. Native starch, on the other hand, has significant disadvantages such as low thermal stability, low surface area, slight water solubility, low molecular weight, rapid degradability in water, and a lack of reaction functional groups, which inhibit it from being utilized as a wastewater treatment adsorbent. As a result, starch must be modified to improve its adsorption efficiency towards various pollutants by changing its chemical surface structure via incorporating functional groups into the starch backbone [6][7].

Starch is composed of numerous hydroxyl groups that are easily modified by the incorporation of functional groups, such as primary amine, carboxylic or sulfonic acid to produce starch-based grafts, hydrogels and beads, polymer nanocomposites, aerogels, nanofibers, and so on, to improve its adsorption capacity for wastewater treatment [6][19]. Owing to the presence of a carboxymethyl functional group, starch derivatives, particularly carboxymethyl starch (CMS), have received a great deal of attention in both research and industry [18]. Starch that has been functionalized, grafted or crosslinked with amine [20][21], carboxylic [22], and carboxymethyl [23] groups along its chains, giving it a high affinity for heavy metal ion removal.

Conventional adsorbents, such as activated carbon, are considered good adsorbents due to their large surface area and excellent adsorption property [24], but starch-based adsorbents have several advantages in the aspects of adsorption capacity, desorption capacity, and lifetime. Starch-based adsorbents have been demonstrated to have a high adsorption capacity for both organic and inorganic pollutants from wastewater when compared to conventional adsorbents owing to their porosity and the presence of many functional groups. Adsorption capacity of starch-based adsorbents can be increased not only by modifying them with functional groups but also by combining them with other materials.

Aside from adsorption capacity, desorption efficiency is critical for reusing utilized starch-based adsorbents. According to Gunawardene et al. [25], modified starch has a desorption efficiency of more than 97%. Starch-based adsorbents are renewable and can be regenerated by washing them with reagent. Reagents for desorption include sodium hydroxide (NaOH) [26], hydrochloride acid (HCl) [26], acetone [27], and more. On the other hand, conventional adsorbents, such as activated carbon, need to be replaced periodically due to their limited lifetime. The use of activated carbon is limited due to its regeneration issues, high cost and not environmentally friendly during its production [24].

In terms of durability and longevity, conventional adsorbents and properly maintained starch-based adsorbents can degrade/decompose in a few months to a few years. However, the degradation rate of starch-based materials is accelerated at high temperatures and high humidity levels, reducing their performance [28]. Extreme operating conditions, such as high humidity, harsh chemical environments, high temperatures, or pressure, will reduce the lifetime of starch-based materials even further [29][30].

2.3. Starch-Based Adsorbents for In situ and Ex Situ Water Remediation

Starch-based adsorbents can be used in the adsorption stage of water treatment. Various adsorbents will be applied at this stage to remove pollutants from the wastewater via adsorption mechanism. Starch-based adsorbents derived from cornstarch [31][32][33][34], rice flour [35], cassava starch [36][37][38], graham flour [35], and potato starch [31][32][39][40] are safe compounds with the potential to be used for in situ water remediation. Starch-functionalized iron oxide nanocomposite, for example, has been utilized to adsorb heavy metal ions from wastewater produced from different industries [41]. The adsorption efficiency of Cd(II) from tap, marine, and industrial wastewater samples ranged from 87 to 93%, 84 to 91%, and 76 to 90%, respectively, whereas the adsorption efficiency of Hg(II) ranged from 69 to 93%, 40 to 89%, and 70 to 94%, respectively. Pb(II) had the maximum adsorption efficiency of 97 to 98%, 92 to 97%, and 93 to 98% for tap, marine, and industrial wastewater samples. Additionally, these starch-based nanocomposites have the potential to be a sustainable adsorbent for metal ions removal from industrial wastewater, marine water, and tap water with 76 to 93%, 70 to 94%, and 93 to 97% of percentage recovery, respectively [41].

The optimum conditions for ex situ water remediation using starch-based adsorbents will vary depending on the type of pollutant, structure (functional group, chain length, etc.) of the starch-based adsorbent, adsorbent dose, pollutant concentration, pH of the treating bath, treatment duration, and agitation speed [42]. Starch-based adsorbents have been found to be effective at removing pollutants at concentrations ranging from a few milligrams per liter to several hundred milligrams per liter [22], as reported in **Table 1**. The initial pollutant concentration is a driving force in overcoming the mass transfer resistance of pollutants between water and adsorbent [43]. Nevertheless, the effectiveness of starch-based adsorbents may decrease at higher pollutant concentrations due to adsorbent surface saturation, increasing the electrostatic repulsion force between the saturated adsorbent and adsorbate in the aqueous solution [44]. Other factors, such as reaction time, pH, temperature, and competing ions in the water, may also have an impact on the performance of starch-based adsorbents [43][45].

In this case, the adsorbent of interest is starch, one of the non-conventional “green” adsorbents that are highly effective at removing a wide variety of pollutants from wastewater. They have higher adsorption capacities and longer lifetimes than conventional adsorbents. Additionally, they are highly advantageous compared to the conventional adsorbents due to their physiochemical nature, abundance, and relatively inexpensive pricing, showing their effectiveness in pollutant adsorption in water treatment processes [46][47].

3. Chemical Structure and Properties of Starch

Chemistry and Properties

Starches with basic chemical formula, $(C6H10O5)n$ is a carbohydrate naturally found in many grains and vegetables, such as wheat, maize, and potatoes [48][49]. Starch is a part of polysaccharide which exists in two structural forms: amylose and amylopectin [50][51]. One of the most abundant polysaccharides in nature, starch provides us with a good supply of additional carbs [52]. The size of starch granules varies, ranging from the sub-micron elongated chloroplast granules to the comparatively enormous oval granules of potato and canna [53][54]. Biosynthesis of starch is a complex process [49][54]. It is also composed of glucose molecules [55] as shown in **Figure 2**.

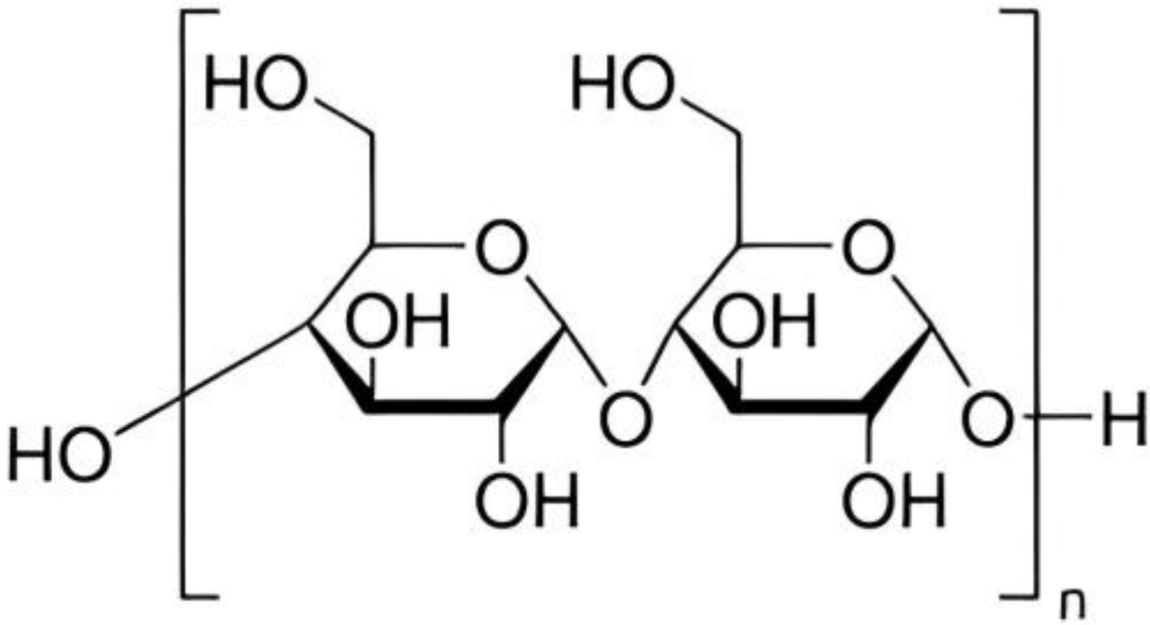


Figure 2. Chemical structure of starch composed of glucose molecules [56].

Amylopectin and amylose are parts of starch that are layered and packed in semi-crystalline and amorphous layers in concentric growth rings [57]. Amylose, which predominantly contributes to the amorphous phase, is a basically unbranched (0.1–0.5% branched) polymer made up of α-(1–4)-linked glucose units [58]. Since amylopectin has more α-(1–6) branch points, it has a more branched structure [58]. Amylose, one of the structural forms of starch, exists as a glucose bonded together in a linear chain or helical chain. Amylose also does not dissolve in water [55]. **Figure 3** shows the chemical structural of amylose.

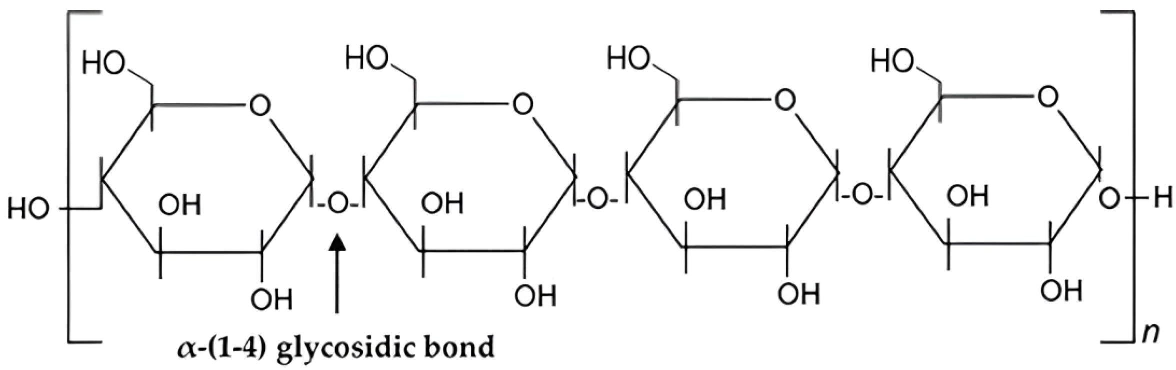


Figure 3. Chemical structure of amylose.

Amylose has an interesting solution property: it can form complexes with iodine and some organic reagents [59]. The amylose/cellulose nanofiber combination has numerous exceptional qualities, including strong heat resistance and storage stability [58]. Starch has a relative amount of amylose which varies according to its source. For example, corn starch has about 28 wt.% compared to cassava starch, with 17 wt.% [60].

Amylopectin is the other structural form of starch. Depending on the botanical origin, the amylose percentage of starch granules varies, although conventional cereal starches typically include between 20 and 30 percent amylose [61]. The ability to control the functions of starch depended on the production of lengthy branch-chains of amylopectin [62]. The ability of long branch-chains of amylopectin to self-assemble structured structures and form complexes with lipids or sodium palmitate resulted in a considerable reduction in starch viscosity and slowing of starch digestion [62][63][64]. Amylopectin is a linear chain of glucose molecules, and it contains a much larger amount of glucose compared to amylose [55]. The structural form of amylopectin can be seen in **Figure 4**.

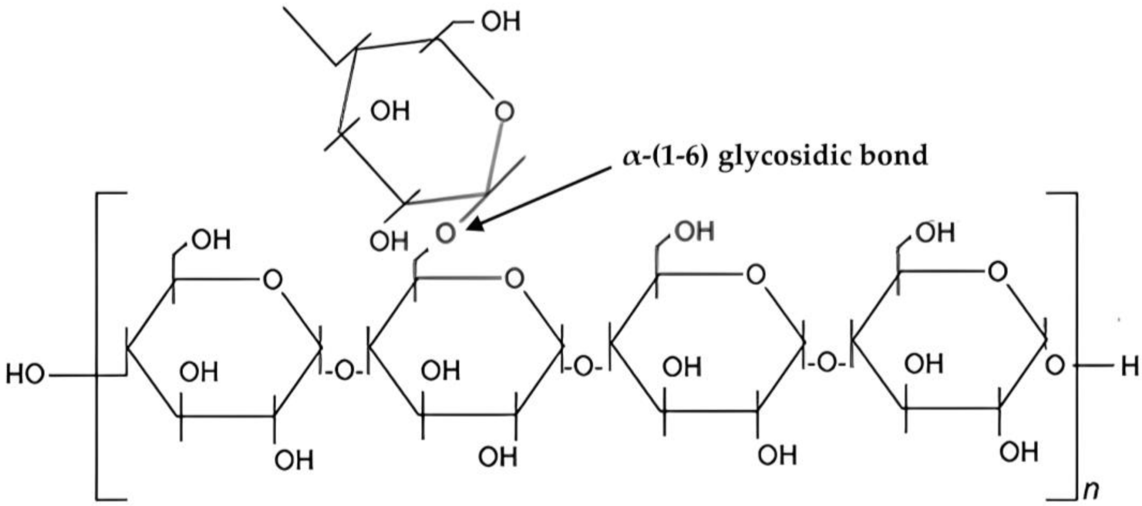


Figure 4. Chemical structure of amylopectin.

4. Applications for Water Treatment

4.1. Removal of Oil and Organic Solvent

There is a significant amount of concern about different contaminants inside the contaminating water, including traditional pollutants like heavy metals and organics, as well as developing micropollutants, personal care products, and substances that interfere with hormones. For purging toxins from wastewater, several researchers are investigating more sustainable materials and methods. The industries that produce chemical extraction, petrochemistry, textiles, and food all produce large amounts of oily wastewater, and this wastewater's excessive discharge has significantly endangered both human health and the environment. These problems can be successfully overcome with starch-based adsorbents for oil and organic solvent removal.

By incorporating nanoparticles into starch cryogel, Wang et al. [65] created a brand new super-hydrophobic sorbent, also known as HMS-SiO_2@MSC, that may be utilized to clean up oil spills. HMS-SiO_2@MSC showed good viability in cleaning the oil slick magnetically and by removing oil underwater. The material's extraordinary ability to absorb oil is in part due to the barrier of trapped air where the chemical inertness of covalent bonding (Si-O-C/Si), and the structural support provided by pore walls. Pore-rich starch or Fe_3O_4 is being mixed with micro-/nanoparticles

(SPF@SC), developed in another study by Wang et al. [66], which was intended to remove occasional oil patches. To clean up occasional oil slicks, magnets remotely control SPF@SC.

4.2. Removal of Pesticides

Given the possible risk to human health, pesticide poisoning of water has drawn a lot of attention. Many academics have recently shown interest in the removal of pesticides from water. Scanning electron microscopy (SEM), FT-IR, X-ray photoelectron spectroscopy, and Brunauer–Emmet–Teller theory (BET) were used to investigate the mesoporous ACS, and it was shown to be highly efficient at cleaning water of contaminants. In fact, it removed 11 pesticides from water better than commonly used adsorbents, such as graphitized carbon black (GCB), activated carbon (AC), C18, and primary secondary amine (PSA) adsorbent. The inclusion of functional groups such as oxygen, nitrogen, and benzene ring bonds dramatically affected adsorption.

Pesticides can be removed via a variety of techniques, including as adsorption, oxidation, enzymatic biodegradation, and photocatalytic degradation. Starch-derived mesoporous activated carbon adsorption is recognized as a highly effective method due to its low starting cost, ease of operation, flexibility, simplicity of design, and insensitivity to harmful pollutants. It is also one of the few methods capable of removing pollutants while remaining unaffected by them. Additionally, it is one of the few methods that can clear contaminants without being harmed by them, making it an extremely helpful tool [67].

4.3. Removal of Heavy Metal Ions

Industrial wastewater and groundwater often contain various inorganic components, including arsenic (As), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), lead (Pb), mercury (Hg), nickel (Ni), zinc (Zn), and others [68]. Modified starches demonstrated substantial adsorption capabilities towards heavy metals by replacing hydroxyl groups with chemically active groups [16]. A wide range of starch derivatives with amino, amide, carboxyl and other groups were synthesized and used in water treatment [69]. Corn starch, for example, can be cross-linked and carboxymethylated to actively capture harmful divalent cations, which include Cu, Pb, Cd, and Hg ions present in water. By distributing 1% of the starch for a couple of minutes and then filtering the starch–metal complex, it was possible to efficiently remove about several hundred ppm of these metal ions from water at a low degree of substitution of carboxymethyl groups [18]. The starch can be easily restored through weak acidic washing, and the success of metal removal depends on avoiding highly acidic metal solutions. Increasing the levels of carboxymethylation and cross-linking can enhance the metal scavenging activity of starch, making it suitable for industrial applications [23][41][70][71][72].

Furthermore, starch can be used for the removal of heavy metal ions by grafting it with various vinyl monomers, including acrylic acid (AA), acrylic amide (AM), acrylonitrile, alkylmethacrylates, methylacrylonitrile, vinyl ketones, and 2-(dimethylamino) ethylacrylate. These polymers, despite their loosely crosslinked network structure and hydrophilic side groups, exhibit remarkable water absorption and retention capabilities [73].

4.4. Removal of Dye

The manufacturing processes of industries, like the leather, paper, and textile industries, release extremely dangerous and carcinogenic chemicals into wastewater. The release of waste dyes from textile finishing poses a significant threat to both natural water resources and human well-being. [36]. Polymers, and more specifically biopolymers, have a wide structure that affords several binding sites for dye molecules. This helps to neutralize the charge that the dye molecules carry, which in turn enables effective precipitation. In applications involving the coagulation of blood, biopolymers are the material of choice since, in contrast to traditional coagulants, they do not pose a threat to human health and have a lower impact on the environment [74].

Starch is a key component in enhancing the quality of the overall nanocomposite due to its amylose chains, which have a strong affinity for anionic dye molecules. A highly recommended alternative method for removing anionic-charged dyes involves using a mixture of starch, chitosan, and glutaraldehyde in specific proportions. This mixture works by utilizing the attractive properties of starch and chitosan to effectively remove the dyes [74]. The combination of starch and chitosan creates electrostatic and hydrophobic interactions that provide benefits in dye removal effects compared to just chitosan alone. These chitosan starch nanocomposites have the potential of 90% in the removal of anionic-charged dye through coagulation-flocculation [75][76][77].

4.5. Removal of Pharmaceutical Pollutants

The discharge of trace amounts of pharmaceuticals into ecosystems is acknowledged as a serious environmental issue, resulting in persistent and immediate impacts on the environment [78]. Starch-Mg/Al-layered double hydroxide (S-Mg/Al LDH) is a synthesized composite utilized in the adsorption of non-steroidal anti-inflammatory drugs (NSAIDs) found in various water and wastewater sources. This adsorbent performs well due to its efficiency and high adsorption rate. S-Mg/Al LDH also showed good reusability performance when tested with optimized experimental parameters.

To remove tetracycline, carboxymethyl-starch-grafted magnetic bentonite [79], starch-stabilized magnetic nanocomposite [80], magnetic starch polyurethane polymer nanocomposite [81], and magnetic starch nanocomposite [82] were created. Shen et al. [79] compared corn-starch-grafted magnetic bentonite (SMB) to carboxymethyl-starch-grafted magnetic bentonite (CSMB) and discovered that the CSMB had a 28% higher tetracycline adsorption capacity compared to SMB. Regarding recyclability, the adsorption capacities of CSMB experienced a decrease of over 20% after the initial cycle due to the destructive effects of nitric acid treatment on some of the functional structures, resulting in a loss of adsorption capacity.

Other pharmaceutical pollutants, such as fluvastatin [83], dox [38], and bovine serum albumin [84], have also been investigated using starch-based adsorbents. The removal of fluvastatin can be accomplished using the magnetic MOF–starch hydrogel created by Mohamed and Mahmoud [83]. The magnetic MOF–starch hydrogel was developed via microwave irradiation and demonstrated several remarkable properties. It exhibits a maximum equilibrium adsorption capacity of 782.05 mg/g, a high surface area of 528.39 m^2/g, a mesoporous structure with a pore size of 2.90 nm, and a highly crystalline structure. Within this system, three types of bonding are expected to occur.

5. Conclusions

The effective use of starch for wastewater treatment comes from its vast availability and sustainability as a natural polysaccharide. In wastewater treatment applications, modified starch products have showed promise in the removal of a range of contaminants, including oil, organic solvents, pesticides, heavy metal ions, dyes, and pharmaceutical pollutants. An example of innovative use of starch-based materials is the development of raspberry-like starch-based polymer microspheres. These microspheres are created through Pickering polymerization and grafting of poly(ethylene imine) (PEI) onto amino-functionalized composite particles. These microspheres not only have the capability to separate oil and water, but they also exhibit simultaneous removal of Cr(VI) and Indigo carmine. The efficiency of oil and water separation is influenced by the dosage of PEI. The resulting composite particles possess unique characteristics, such as rough structures, distinctive surface wettability, and positive charge. This combination enables them to simultaneously separate water-in-oil (W/O) and oil-in-water (O/W) emulsions within a specific dosage range of PEI. Moreover, the amino-functionalized composite particles carry a positive charge, which enhances their ability to effectively absorb anionic water-soluble pollutants. The removal rate of these pollutants during the oil/water separation process can reach nearly 90%.

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