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Review

Sustainable Starch Strategies: Nano and Macro Adsorbents for the Detoxification of Synthetic Dyes and Heavy Metals

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Abstract: The research being conducted explores environmentally friendly techniques for heavy metal and synthetic dye detoxification from aquariums via nano- and macro adsorbents based on starch. In exposure to the urgent demands for sustainable wastewater treatment solutions, the research effort focuses on the development and evaluation of materials made from starch that have enhanced adsorption abilities. The effectiveness of developing and evaluating macro- and nano-sized starch composites and starch-based adsorbents in facilitating the elimination of heavy metals and synthetic colours is determined. The review includes a thorough examination of equilibrium traits kinetics, and adsorption processes, also takes into account how these sustainable starch-based products could be employed in real-world environmental remediation scenarios. The aforementioned findings offer significant additional knowledge regarding how to develop and implement starch-based adsorbents for the long-term and effective detoxification of heavy metals and synthetic colours compared to water.

***Keywords*:** starch-based materials, adsorption, heavy metals, dyes, eco-friendly

1. Introduction

Water contamination is typically caused by activities within the industrial sector[1]. The trash generated by industries such as food coloring, paper, plastic, textiles, leather tanning, and cosmetics[2] releases from 2 to 20% of dyes into wastewater[3]. The intricate aromatic structure of these synthetic pigments makes them resistant to heat, light, reducing agents, and biodegradation[4]. The chemicals that cause cancer and mutagenicity, their impact on human health, and their non-biodegradable nature on marine life[5]. Dyes can lead to a number of health issues, including hepatitis, allergies, hives on the skin, and anomalies in the central nervous system of mammals[6]. In a similar vein, dissolved colours in water decrease the activities of photosynthesis in algae and aquatic plants as well as the disintegration of the food chain[7]. Further, human activity and various industrial activities can contaminate the water bodies with heavy metals[8]. Human activity introduces heavy metals into the marine environment, and seaweed quickly accumulates large concentrations of these elements. In the end, they affect humans by becoming a part of the food chain[9]. Anemia, nervous system disruption, liver and kidney damage, and anemia are only a few of the illnesses brought on by heavy metals[10],

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tumors[11], and dementia[12]. The bulk of the heavy metal is absorbed by fish gills, that results in damaged gills and liver in fishes, eosinophilia, malformations, skeletal and bronchial illnesses, reproduction, Minamata, and affects the activity of the catalyst for for oxidative metabolism[13]. These are the different issues causing by heavy metals in fish[14]. Dye and extraction of heavy metals from wastewater can be achieved thus far by employing a range of technologies, such as membrane filtration, adsorption, ozonation, chemical oxidation, photo-catalytic degradation, biological treatment, ion exchange, and the Fenton process[15]. Because adsorbents are widely available, the adsorption process is straightforward, and the other ways are very effective, this is the most advantageous adsorption approach[16]. Examples of materials regarded as adsorptive comprise carbon composites, sawdust, fly ash, zeolite, clay, activated carbon, and charcoal have all been studied in the literature for their ability to remove dyes and heavy metals. However, because these adsorbents were large and non-renewable, they did not gain much traction. Now, however, biopolymers-especially those made of cellulose, chitosan, and starch-have completely replaced these adsorbents because of their rationality, affordability, and renewable nature. Glucose molecules bound together by glycosidic bonds make up the majority of the molecules that make up starch. Accessible, reasonably priced, and biodegradable are just a few of its numerous advantages.

Worldwide freshwater shortages are becoming more acute as a result of the fast-growing global population, changing climate, and industrial expansion. These factors have also had a substantial impact on water quality. A wide variety of pollutants greatly contribute to the depletion of freshwater resources[17]. The principal culprits of pollution are industrial pollutants like crystal violet. The industries that produce pulp and paper, paint and varnish, food, cosmetics, leather, and textiles are among those that are the source of these toxins[18]. A recent estimate estimates the yearly worldwide production of dyes at over 70 lakh pounds[19]. The environment and public health might be at risk if this color made from industrial waste gets into the water system. When untreated wastewater containing color is dumped straight into natural water bodies, it adversely affects the capacity of aquatic ecosystems to perform photosynthesis[20]. It embraces metals as a consequence of fish species and other aquatic life becoming mutagenic or teratogenic[21]. Methylene blue (MB), methyl orange (MO), methyl red, disperse Violet 26, rhodamine B (RhB), and congo red (CR) are the most commonly employed dyes. Moreover, colours in the environment can have mild to severe negative effects on human health, including dermatitis, allergies, kidney disease, and mutagenic and carcinogenic outcomes[22]. As indicated by reports, dyes based on chromium often have a complex structure and can cause cancer in humans[23]. Dyes thus get discharged into the environment and contaminate water bodies, which in return affects aquatic life, human health, and water quality Table 1 explains how dyes affect living organisms eco-toxicologically.

Table 1. Categories of dyes, instances, uses, water solubility, and Eco-toxicological effects

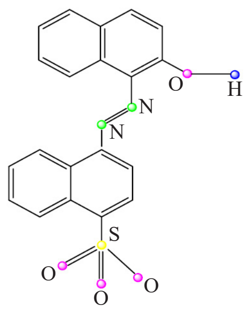
Types of dyes	An illustration of a dye's chemical composition	Dye examples	Employing dye	Water-soluble nature	Impacts of ecological toxicology	Ref.
Acid Dye	 Acid Red 88	Acid yellow 36 Acid orange 7 Acid blue 83	Industries: nylon, silk, and modified acrylics; textile, leather, and medicinal	solubility in water	Effects that can include nausea, vomiting, loose stool, malignancy, and abnormalities.	18

Table 1. (cont.)

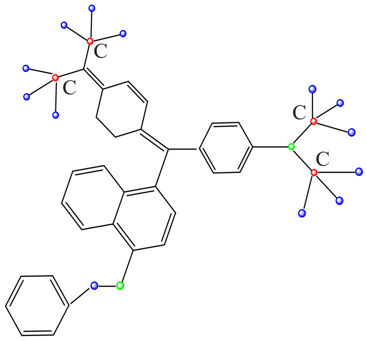
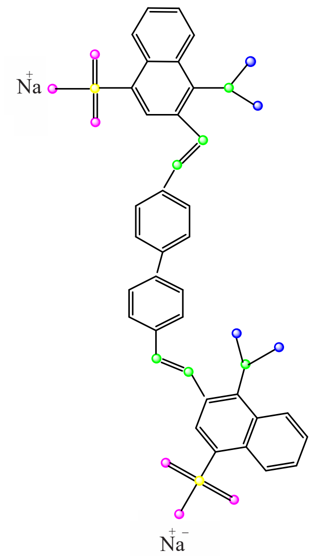
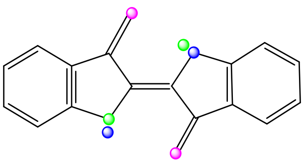
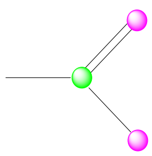
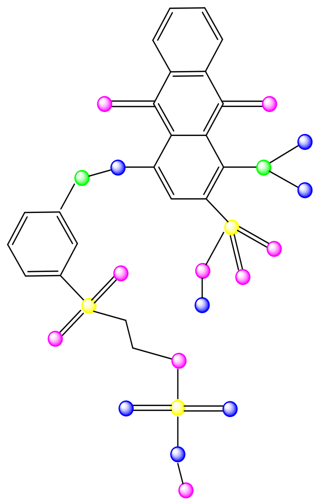
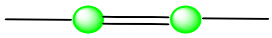
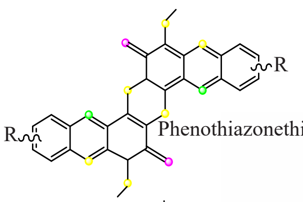
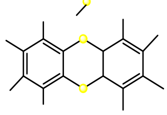
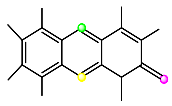
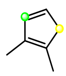
Types of dyes	An illustration of a dye's chemical composition	Dye examples	Employing dye	Water-soluble nature	Impacts of ecological toxicology	Ref.
Basic dye	 Basic blue 26	Methylene blue (MB), Basic red 1, or rhodamine 6G, Basic yellow 2	Nylons, modified polyesters, paper, and poly-acrylonitrile modified	Soluble in water	inflicting harm to the flora and wildlife and changing the chemical and physical characteristics of aquatic environments	24
Direct dye	 Direct red 28	Congo red (CR), Direct red 28, Direct black 38	Product: shading paper	solubility in water	dermatitis, carcinogenic, mutagenic, and toxic to marine organisms and plants	25
Vat dye	 Vat blue 1	Vat blue 1, Vat acid blue 74	Natural fabric, cellulosic rayon fibres, indigo, and insoluble pigment	Water soluble	Life-threatening effects include dermatitis, allergic conjunctivitis, rhinitis, and other allergic responses, as well as a reduction in the quantity and purity of water resources, such as lakes and rivers.	26
Nitro dye	 Chromophore of nitro dye	Naphthol yellow (II)	Dye wool		In spite of inflicting major degradation to water supplies, such as rivers and lakes, allergic reactions can have dangerous side effects such as dermatitis, rhinitis, allergic conjunctivitis, and other allergic reactions.	18

Table 1. (cont.)

Types of dyes	An illustration of a dye's chemical composition	Dye examples	Employing dye	Water-soluble nature	Impacts of ecological toxicology	Ref.
Reactive dye	 Reactive blue 19	C.I. reactive red 120, C.I. reactive red 147, C.I. reactive blue 19	Wool, silk, and cellulosic fibres dyeing		Elevated and undesirable concentrations of dissolved particulates in the effluent Allergy response in the upper respiratory tract, eyes, skin, and mucous membrane	18
Azo dye	 Chromophore of Azo Dye	Direct Black 22, Disperse Yellow 7, Acid Orange 20, Methyl red, Methyl orange (MO), Trypan blue	textile sector for hues and dyeing procedures		Causes cancer in both people and animals. It damages the skin, digestive system, and eyes when consumed or breathed. Impacts aquatic life when overexposed.	27, 28
Sulphur dye	 Phenothiazonethianthrone  Thianthrene  Thiazone  Thiazole	Sulfur brilliant green, Sulfur blue, Sulfur Black 1, Leuco Sulfur Black 1, Phthalic anhydride	Dyeing cellulosic fibres and cotton	Water insoluble	Itchy or clogged nostrils, sneezing, aching eyes, and skin irritation are all associated with cancer.	18

So, since relating to research on dye wastewater remediation, some of the main areas of interest are filtration, adsorption, ion-exchange, electrocoagulation, coagulation/flocculation, activated sludge processes (ASP), sequencing batch reactors (SBR), membrane bioreactors (MBR), moving bed biofilm reactors (MBBR), and established wetlands (CW)[29]. Charged suspended and colloidal contaminants are destabilised during the coagulation process[30]. The process of electrocoagulation uses a direct current source and iron or aluminum metal electrodes dipped in water tainted with dye. Among the coagulated species that metal ions produce at particular pH values are metal hydroxides, which accumulate and stabilise suspended particles known as precipitates while also absorbing dye molecules[29]. The emergence of solid hyperlinks between the dye molecules and the resins sets dye apart from wastewater[31]. Adsorption-oriented pigments (AOPs) have been effectively utilised for the treatment of dye wastewater, encompassing Fenton, ozonation, ultrasonic, anodic oxidation, ultraviolet/hydrogen peroxide (UV/H_2O_2), and photocatalytic processes. A breakdown process that produces active oxygen pollutants (AOPs) occurs with certain pollutants[32].

As seen by Figure 1a, which displays, because so many papers have been authored regarding different contemporary physicochemical and biological treatment methods, adsorption is regarded as one of the most significant and effective decontamination procedures. Recyclable facilities, mechanical stability, high efficiency and/or selectivity, simplicity, speed, and cheap cost are all considered advantages of this method[33]. Adsorption is a widely employed technique for extracting heavy metals, dyes, and arsenic, among other sorts of contaminants, from wastewater[34]. Furthermore, Figure 1b features a pie graphic that illustrates the volume of available literature on dye removal techniques utilizing various adsorption tactics. The goal of the current investigation is to extract dye from contaminated water by looking into potential applications for various adsorbents. Traditionally, a variety of adsorbents, including activated carbon, carbon-based, metal oxide-based, bio-adsorbent, metal-organic framework (MOF), and polymer-based materials, are used to remove dye from polluted water[35]. These adsorbents incorporate high surface volume ratios, strong reactivity, plenty of active sites, low cost, ease of fabrication, huge effective surface area, numerous applications, reusability, and remarkable efficacy in treating refractory chemicals, among other benefits[36].

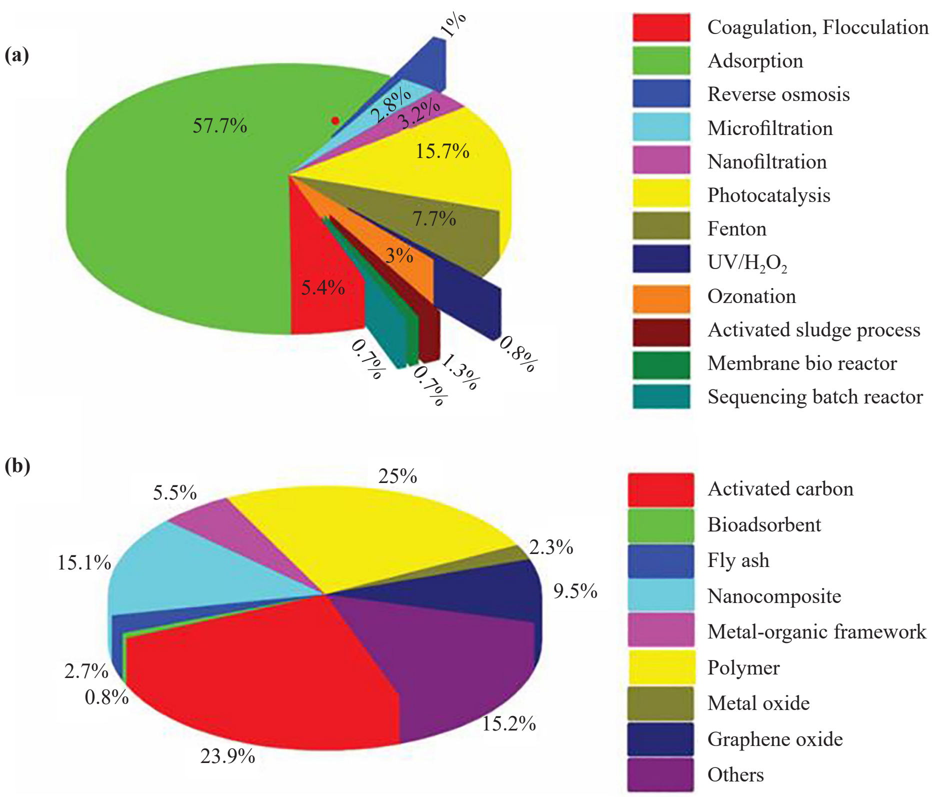


Figure 1. A pie chart indicating the percentile of research for (a) various biological and physical chemical techniques comprising hue removal steps. The acronyms of every procedure as they show up in the plot, dye, water, and treatment serve as the keywords. (b) adsorption methods employing distinct adsorbents. Key terms: each type of adsorbent identified in the plot, adsorption, dye, and water

With the implementation of starch-based adsorbents, dye extraction from wastewater may now be completed successfully. The conditions under which the adsorbents were tested, their adsorption capacity, features, ranging and mode of removal, are displayed in Table 2 and 3.

Table 2. Enumeration of starch-based adsorbents for dye removal

Adsorbent	Dyes	Adsorption capacity	Ref.
Silica-sand anionized starch composite (CMS-SS)	Methyl blue, Crystal violet	653.31 mg/g and 1,246.40 mg/g	37
Carnation based starch-particles (SPs)	Methylene blue	716 mg/g	38
Bifunctional hydrogel of starch with 2-acrylamido-2-methylpropane-1-sulphonic acid and dimethylaminoethyl methacrylate	Astrazon red	600 mg/g	39
Hydrogel of cross-linking starch with acrylic acid	Methylene blue, Congo red	64.73 mg/g, 133.65 mg/g	40
Hydrogels of hydroxyethyl starch/p(3(acrylamidopropyl) trimethyl ammonium chloride) and hydroxyethyl starch/ p(sodium acrylate)	Methyl violet, Methyl orange	238.1 mg/g, 185.2 mg/g	41
Starch-coated Fe_2O_3 NPs	Optilan blue	125 mg/g	42
Starch and hen feather silver nanoparticles	Rhodamine B	48.6 mg/g, 56.53 mg/g	43
Succinylated starch nanocrystals	Methylene blue	84 mg/g	44
Starch malonate (MA-St), starch glutarate (GA-St) and starch valerate (VA-St)	Methylene blue	74.49 mg/g, 75.38 mg/g and 80.25 mg/g	45
Carboxymethyl Starch-g-Poly(vinylpyrrolidone)	Rhodamine 6G	363.95 mg/g	46
Starch-polyvinyl composite	Reactive black 5, Reactive orange 131	605 mg/g, 539 mg/g	47
Starch/CTA-bentonite and starch/CTA-magatiide	Methylene blue	89.82 mg/g, 76.59 mg/g	38
Ethylenediamine/glutaraldehyde-modified starch (SEG)	Direct red 23 (DR23), Acid blue 92 (AB92)	129.87 mg/g, 147.05 mg/g	48
Cationic cross-linked starch	Golden yellow SNE	208.77 mg/g	49

Table 3. Leveraging starch-based composites to eliminate additional dyes

Adsorbent	Surface area (m^2/g)	Dye	Adsorption conditions					Adsorption capacity (mg/g)	Isotherms/ kinetics	Mechanism	Ref.
			pH	Time (min)	Conc. (mg/L)	Adsorbent dosage (g/L)	Temp (°C)				
ZnSe nanoparticles loaded on activated carbon employing starch-cabbed starch (ST-Zn-Se-NPs-AC)	-	BF	7	6	15	12 mg	25	222.72	Langmuir/ PSO	Intra-particle and boundary layer diffusion, complexation, or ion exchange	50
Poly(N,N-dimethyl acrylamide) hydrogel grafted with starch (St-g-PDMAm)	-	ARB	1	60	350	2	ambi-ent	104	Langmuir/ PSO	Electro-static Interaction & chemisorp-tion	51
Porous starch xerogels modified with mercaptosuccinic acid (PSX/MSA)	-	GY	-	8 h	100-400	-	-	72	frendlich/ PSO	H-bonding and pore diffusion	52
Amine-crosslinked Starch (ACS)	-	BB	-	-	-	-	-	1287.7	Langmuir/ PSO	-	53

Table 3. (cont.)

Adsorbent	Surface area (m^2/g)	Dye	Adsorption conditions					Adsorption capacity (mg/g)	Isotherms/ kinetics	Mechanism	Ref.
			pH	Time (min)	Conc. (mg/L)	Adsorbent dosage (g/L)	Temp (°C)				
Ethylenediamine Modified starch (CAS)	-	A010	4	1.5 h	800	0.05 g	25 ± 1	0.591	Langmuir/ PSO & PSO	Electrostatic attractions and H-bonding	54
FeS@Starch-derived carbon composite derived from manganese residue (MR-FeS@SC)	51.5	ST	7	240	100	0.8	30	93.52	langmuir/ PSO	Chemisorption,	55
Corn starch	-	Rh-B	6.02	30	50	0.5 g/ 50 ml	30	1.176	Freundlich/ PFO and Elovich	Diffusion between particles, H-bonding, and chemisorption	43

Anyone and virtually every green plant emit an insoluble organic substance in alcohol, cold water, or other solvents that are white, granular, and tasteless. notably, starch has the chemical formula $(C_6H_{10}O_5)$[56]. Integrating amylose and amylopectin, it is generated up of glucose units coupled by the 1, 4 and 1, 6 linkages. All of the lot (iso)enzymes and proteins that make up the whole starch metabolism are far simpler than this simple chemistry implies[57]. Starch is a polysaccharide that is made up of the two glucan subtypes found in plant granules, amylose and amylopectin. Amylose and amylopectin occupy 98-99% of the dry weight of the starch granules. Amylose is a straight-chain polymer of D-glusoce units; amylopectin a branched chain polymer. In comparison, various varieties of rice contain varied quantities of amylopectin[58]. The beneficial effect of starch in terms of adsorption is low. Researchers are making an effort to solve this problem by trying to substitute other functional groups for the hydroxyl groups in starch. Hence, several techniques to modify starch have been documented in scholarly works. Figure 2 appears that the usual architectures of amylose and amylopectin.

For green plants to retain energy for extended periods of time, they need granules generated from renewable starch. Densities of around 1.5 g/cm^3 have also been recorded for the semi-crystalline, closely packed starch granules. Using cryo-X-ray ptychographic tomography, a density of 1.36 g/cm was found for fully hydrated, amylose-free B-type Arabidopsis leaf starch. The partially visible "blocklets" have been observed using partial starch granule digestion, atomic force microscopy, scanning electron microscopy, small-angle neutron and X-ray scattering methods. Their ellipsoidal-shaped cylindrical form has a diameter that ranges from 50 to 500 nm[59]. Starch is a widely dispersed, cheap, renewable, biodegradable, and spontaneously occurring biopolymer that may be found in a wide range of plants. Like the bulk of other plant material, starch makes up almost all plant tissue, including that of leaves, fruits, pollen grains, roots, and stems. Many of the demands of contemporary technology are satisfied by starch[60].

In recognition of starch's beneficial qualities, which include adhesion, coating, thickening, gelling, and encapsulating, it may be used in a variety of food processing applications. The most significant impacts of starch are pasting, retrogradation, and gelatinization[61]. Because it has a multitude of active hydroxyl groups on its surface, starch have a flexible structure, allowing various kinds of modification. When a starch undergoes processing to alter its molecular size, add new functional groups to its molecules, or alter the properties of its particles, all of which alter the starch's inherent attributes, the term "modified starch" is used[62]. Using data from the experiments, Figure 3 shows each stage of the starch granule's hierarchical structure.

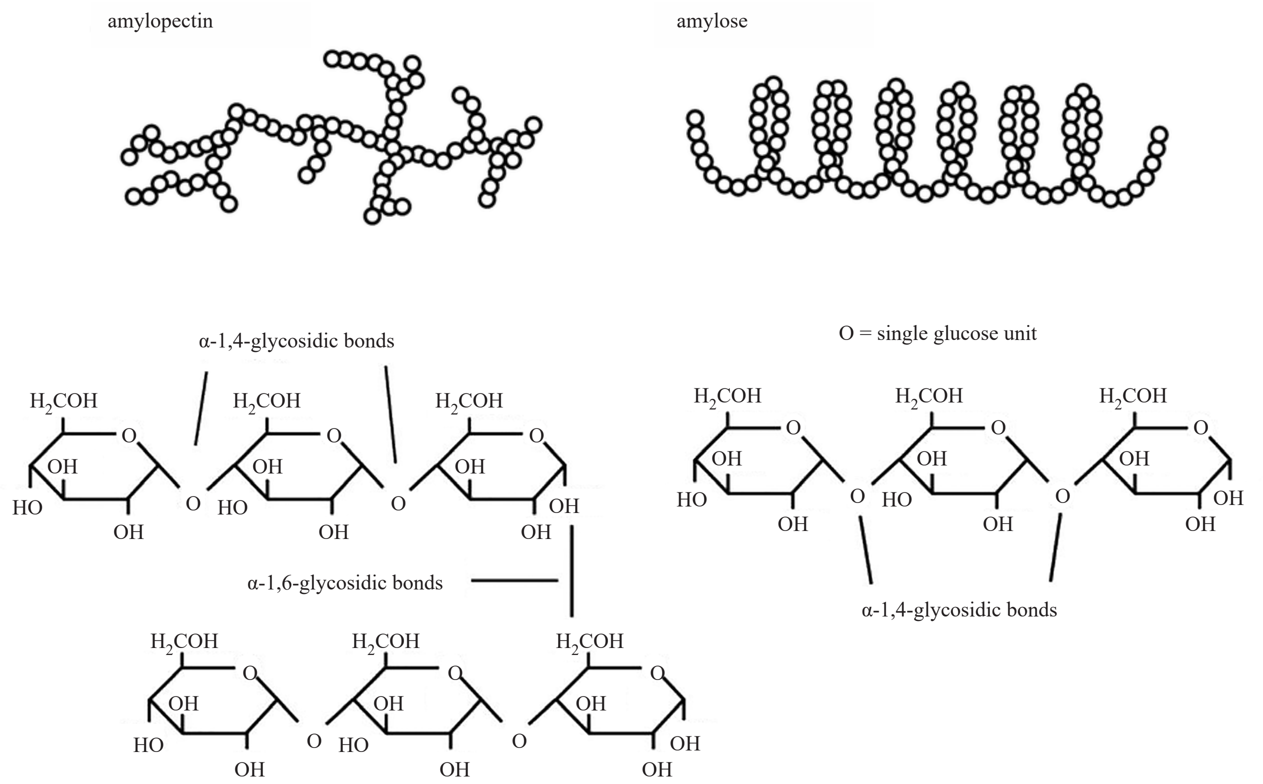
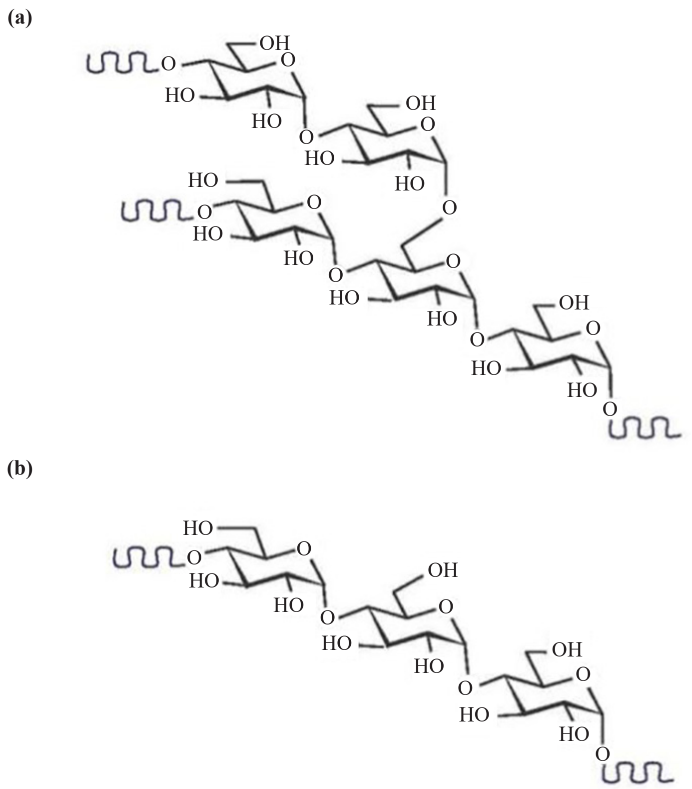


Figure 2. Structural composition of amylose and amylopectin



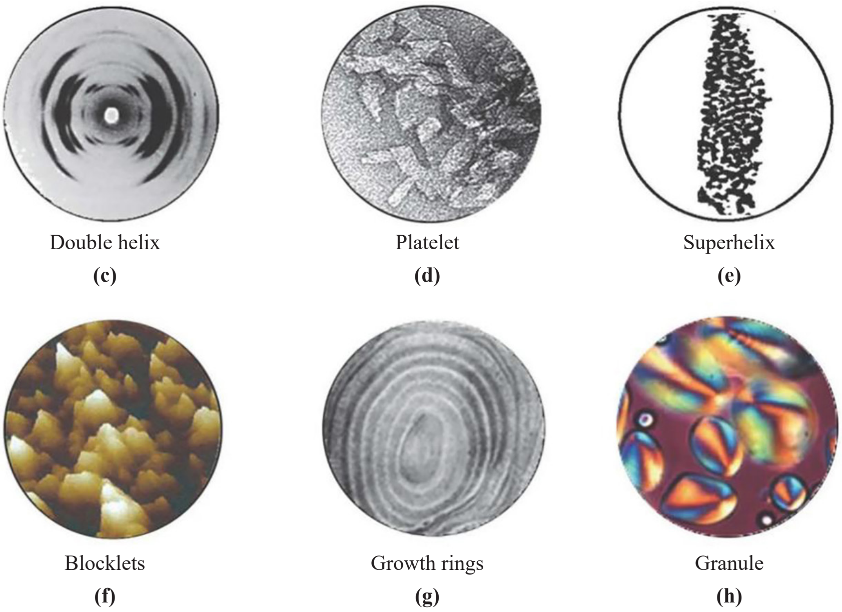


Figure 3. Trial information indicates the starch granule's hierarchical structural level. Using ChemDraw, the components of starch are (a) amylopectin and (b) amylose. In (c), a double-helical structure can be determined by the X-ray fibre diffraction pattern. A Maltese cross is seen extending from the hilum (d); a transmission electron micrograph (e) shows crystalline platelets made of starch hydrolyzed in an acidic solution; granular starches exposed to iodine vapour in humid environments show 'blocklets' measuring 10-500 nm in diameter (f); alternating semi-crystalline and amorphous 'growth rings' measuring 100-400 nm in thickness (g, h)[59]

The physicochemical traits observed in oxidized starches, such as decreased viscosity and heightened gelatinization enthalpy, illustrate how chemical alterations impact the properties of starch[63]. The enhanced stability, swelling volume, solubility, and water binding capacity seen in hydroxypropyl derivatives of cassava starch underscore the influence of derivatization on starch characteristics[64]. Methods for modifying starch, such as heat-moisture treatment and esterification, change its physicochemical characteristics, broadening its range of potential uses[65]. To sum up, starch and its derivatives offer versatility across food, packaging, and materials science fields. Grasping the modification and functional traits of starch is crucial for maximizing its utility across diverse industrial sectors.

2. Starch modification

Native starch has only a small number of possible uses due to its absence of persistent functional groups. In order to improve starch efficiency, modification is required. Different functional groups will need to be incorporated into the backbone of starch to alter it. Water contaminated by textiles can benefit from the use of reformulated starch[66a]. Enzymatic, chemical, and physical methods can be routinely employed for adjusting starch in order to increase the number of advantageous properties and physical methods can be routinely employed for adjusting starch in order to increase the number of advantageous properties[66b].

2.1 *Chemical modification of starch*

With no change to the chemistry or size of the granules, the chemical modification makes starch more physiologically desirable by adding more chemicals or functional groups[67]. Using certain chemical processes, functional groups including phosphate, aldehyde, acetate, and carboxyl were added to starch particles in order to modify the modified starch's properties, including drug release, sorption capacity, and rate of biodegradation. Hence, it is projected that chemical modification would change how starch functions and be utilized to improve some technical elements of food processing, such as paste behavior and gelatinization. In a similar vein, resistant starches (RS) with anti-diabetic and anti-cancer properties can be produced by chemical starch modification[68]. In the process of modifying starch, common methods include oxidation, and cross-linking.

2.1.1 *Oxidized starch*

The hydroxyl groups in the starch polymers are converted to carbonyl and carboxyl groups in this most popular form of starch modification, and the starch molecules are depolymerized by cleaving glycosidic bonds[69]. The swelling power, pasting temperature, retrogradation propensity, and viscosity of oxidized starches are generally lower. Bread conditioners, thickeners, emulsifiers, gelling agents, drug delivery agents, stabilizers, and gum Arabic substitutes are among the applications for oxidized starches[70]. A certain quantity of oxidizing reagent is reacted with starch at a regulated temperature and pH to create oxidized starch, which finds widespread application in several industrial domains. Sodium hypochlorite, bromine, periodate, permanganate, hydrogen peroxide, and ammonium persulfate are some of the oxidizing agents that have been used to treat starch oxidation[71]. Figure 4 shows the oxidation mechanism of starch.

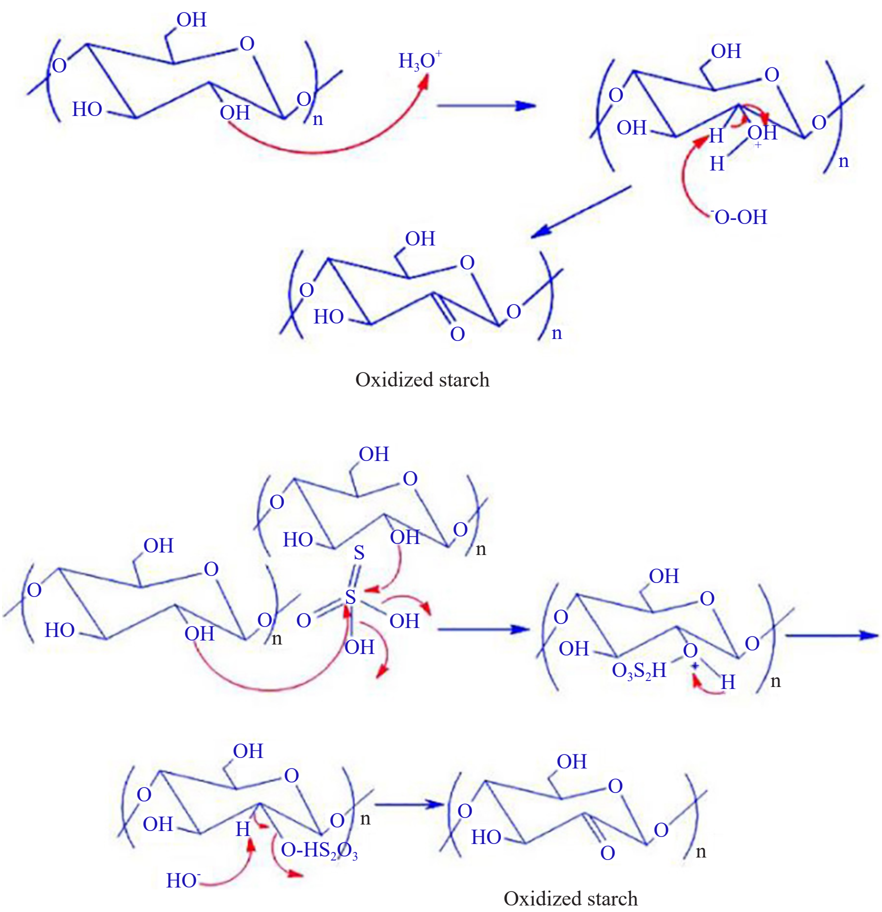


Figure 4. Oxidation mechanism of starch[72]

2.1.2 *Cross-linked starch*

Cross-linking in polymers refers to the process of creating chemical side bonds between different chains. A variety of well-known cross-linking reagents, include sodium tripolyphosphate, sodium trimetaphosphate, and phosphorus rus oxychloride epichlorohydrin[6]. Chemical linkages that join polymer chains to generate bridges between intermolecular hydrogen bonds are what create cross-linked starch[73]. Starch that has undergone crosslinking can provide the product the necessary functional qualities. A number of variables affect the effectiveness of the crosslinking process, including the reagent's composition and concentration, the starch supply, reaction duration, temperature, and pH[74]. The reactions of some of these reagents are depicted in the Figure 5 below.

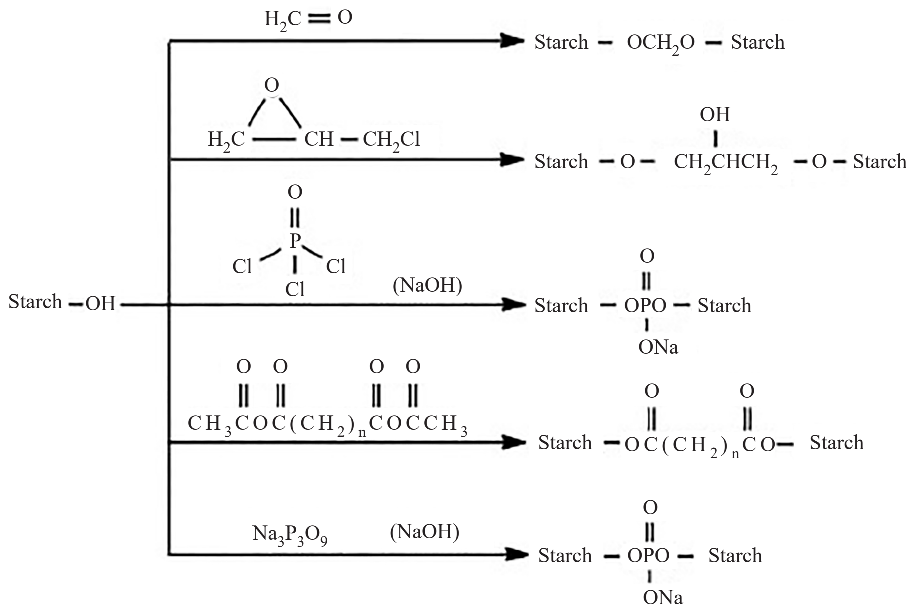


Figure 5. Cross-linking of starch[6]

2.1.3 *Esterification of starch*

When starch is esterified, the reaction either happens at the outside surface of the starch molecule, maintaining the internal crystalline structure, or it happens on the whole starch chains to generate traditional starch esters. An organic acid (RCOOH) and an alcohol (ROH) are combined in this process to create an ester (RCOOR) and water[75]. During esterification, side chains are added to assist produce thermoplastic end products, and ester groups function as internal plasticizers. Starch may easily participate in the esterification process since it has three hydroxyl groups[76]. Organic acids (anhydrides and chlorides) and inorganic acids (sulphate and phosphate) can be used to treat starches to create esterified versions. Higher transparency and viscosity are exhibited by starch phosphates or inorganic starch esters. Because of these qualities, starch phosphates can be used in medication administration as a thickening, adhesive, stabiliser, and bulking agent[77]. The synthesis of esterified starch is shown in Figure 6.

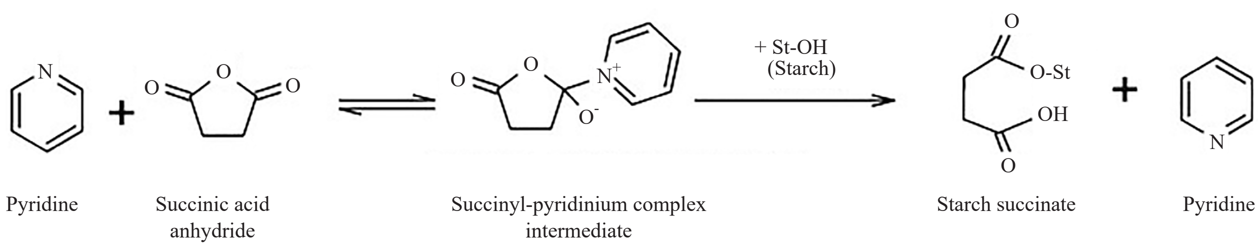


Figure 6. Synthesis of esterified starch

2.1.4 *Grafting*

Starch, like other biopolymers, is grafted for application in a variety of domains, including medication delivery, tissue engineering, and wastewater treatment. For the production of graft co-polymers, three techniques are often used: grafting onto, grafting from, and grafting through. The grafting onto method is connected to the interaction between functional groups of two distinct polymers. Grafting from approach refers to grafting in which a polymer with a particular functional group initiates the polymerization of vinyl monomers. The copolymerization of macromonomers is used in the grafting via method[78]. Among the aforementioned methods, the grafting from the approach is the most commonly employed because of its high grafting yield, which is related to the facile availability of reactive groups to the chain ends of the establishing polymers[79,80].

2.2 *Physical modification of starch*

Starch has to be challenged to a range of physical stresses, incorporating ultrasonic waves, reverberated electric fields, radiation, moisture, pressure, pH, and milling, in order to physically alter its morphology and three-dimensional structure[81]. The adjustment of starch properties through physical means doesn't entail altering its chemical structure. Diverse physical modification techniques have been investigated to improve starch's utility and adaptability across various industries. These methodologies encompass hydrothermal treatment, microwave exposure, ultraviolet (UV) and gamma irradiation, highpressure processing, high-pressure homogenization, ultrasound application, and milling. Each of these methods offers unique avenues to modify starch, tailored to specific industrial needs. For instance, hydrothermal treatment involves subjecting starch to heat and moisture to fine-tune its viscosity and gelatinization properties, while microwave treatment provides swift and uniform heating, particularly useful for certain applications. Ultraviolet and gamma irradiation can prompt cross-linking within starch molecules, bolstering their stability and strength. Conversely, high-pressure treatment can adjust starch's rheological properties sans chemical alterations. High-pressure homogenization reduces starch particle size, enhancing dispersibility and texture. Ultrasound treatment disrupts starch granules, affecting changes in its functional attributes. Lastly, milling breaks down starch granules mechanically, altering their size and structure. Collectively, these methods furnish a diverse toolkit for customizing starch to meet the specific demands of different industries[82]. There has been a thorough examination of how physical modification methods affect the physicochemical and functional attributes of starch. It has been emphasized that physical modification leaves the chemical structure of starch unchanged, setting it apart from chemical modification techniques that entail introducing functional groups into the starch granules[83]. Physical modification of starch plays a crucial role in customizing its properties to fulfill particular industrial needs, particularly in sectors like food processing, bioplastics, and packaging[84]. Physical modification of starch is integral to the creation of thermoplastic starch, which has garnered interest for its potential across diverse applications such as packaging and material science[85].

Pre-gelatinization is the most common physical method of starch modification. Basically, pre-gelatinized starches (PGS) is a starch that has been pre-cooked and dried which is formed by complete gelatinization of starch by drum and spray drying, an extrusion process and then drying of native starches. For preparing PGs, drum drying is the most commonly used method to modify starches at industrial scale[86]. Hydrothermal treatment represents a physical modification wherein the physicochemical properties of starch are altered without compromising the granular structure of the starch[87]. This transition occurs as the starch polymers shift from the amorphous to the semicrystalline region[88]. This physical alteration relies on the interplay of moisture, temperature, and heating duration to shape the characteristics of starch. It proves effective in restructuring molecular chains, achieved by immersing starch granules in abundant water or at moderate water levels, typically exceeding 40% water (w/w), over a specific timeframe. This occurs at a temperature surpassing the glass transition temperature but remaining below the gelatinization threshold[89].

Recent studies have explored novel techniques for modifying starches sourced from various plants. These methods include superheated starch, iterated syneresis, thermally inhibited treatment (dry heating), osmotic pressure treatment, multiple deep freezing and thawing, instantaneous controlled pressure drop (DIC) process, mechanical activation with stirring ball mill, micronization in vacuum ball mill, pulsed electric fields (PEF) treatment, and corona electrical discharges. These advancements in physical modification methods are detailed in Table 4.

Table 4. Recent physical modification of starch

Physical Modification	Ref.
Superheated starch	89
Iterated syneresis	90
Thermally inhibited treatment	91
Osmotic-pressure treatment	92
Multiple deep freezing and thawing	124
Instantaneous controlled pressure	93
Drop (DIC) process	94
Mechanical activation-with stirring ball mill	95
Micronization in vacuum ball mill	96
Pulsed electric fields treatment	97
Corona electrical discharges	98

2.3 *Enzymatic modifications of starch*

The enzymatic modification tackle yields an alternative starch structure. Branch chain length, amylose/amylopectin ratio, and molecular mass distribution can all be impacted by enzymatic interactions with gelatinized starch. In an effort to improve product quality, produce food components, and process food more efficiently, the food industry has experimented with a number of innovative enzymatic modifications of starch[99]. For the production of modified starch, enzymatic variants have mostly supplanted chemical and physical techniques since they are safer, more renewable, and better for food consumers. There are several uses for native starches in food, paper, textile, and other sectors because of the enzymatic alteration that changes their viscosity, solubility, and gelation[100].

3. Heavy metal adsorption by starch

The association between heavy metals and starch stems from starch's capability to capture heavy metal ions in water solutions, preventing their precipitation and assisting in their environmental removal. Heavy metal adsorption is thought to be caused by the chelating inclined and physical entrapment of the metal ions. Table 5 provides an overview of how starches may be modified and their adsorption properties changed for the heavy metal adsorption.

Starch-based binding agents have proven effective in immobilizing heavy metal ions, especially under alkaline conditions, showcasing starch's potential in sequestering heavy metal ions[113]. Moreover, exposing duckweed cultures to heavy metals has been demonstrated to hinder growth and trigger starch accumulation in a manner that correlates with the dosage, suggesting a direct link between heavy metal exposure and starch buildup[114]. To conclude, existing literature underscores a robust correlation between heavy metals and starch. Starch exhibits the capability to both bind heavy metal ions and accumulate in response to exposure to heavy metals. Moreover, it can be chemically modified to augment its capacity for sorbing heavy metals. These observations highlight starch's promising role as a cornerstone for research endeavors aimed at devising efficient strategies for removing heavy metals from aqueous environments.

Table 5. Implementing modified starches for heavy metal adsorption: an overview of the literature

Botanical ancestry	Sorts of starches that have undergone chemically altered	Shifts in the physical-chemical characteristics	Heavy metals adsorbent	pH	Isotherms	Kinetic models	Adsorption capacities (mg/g)	Removal %	Ref.
Patato	Starch phosphate	The adsorbent portion is retained after phosphorylation is crystalline in appearance.	Pb(II)	5.5	NR	NR	NR	99.9%	101
Corn	Dibenzo 18 crown 6 grafted starch	The grafted starch has open pores and rough, uneven surfaces.	Ni(II) Cd(II) Cu(II) Zn(II)	6.5	Freundlich	Pseudo second order	182.5 368.5 385.0 377.5	87% 85% 94% 90%	102
Tapioca	Suucinylated starch nanocrystals	When succinylation occurred, DS rose. Surface-COOH groups are plentiful.	Cu(II)	5.0	Freundlich	Pseudo second order	95%	NR	44
Corn	Oxidised starch nanoparticles	A rise in the oxidised starch's carboxyl content. With increasing oxidation degree, enthalpy dropped.	Cu(II) Pb(II)	7.0	Langmuir	Pseudo second order	40.5 32.9	NR	103, 104
Cassava	Poyethylene-graft-poly(acrylic acid)-co-starch/ organomontmorillonite Hydrgel composite	Retaining its crystalline structure Organomontmorillonite's exfoliation.	Pb(II)	4.5	Langmuir	Pseudo second order	430	NR	105
NA	Nanoscale zero valent iron stabilised starch and carboxemethyl cellulose	Particles stabilised with starch were less distinct and nonuniform. Dendritic structures were produced by particles.	As(III) As(V)	5.0	Langmuir	Pseudo second order	12.2 14.0	99% 99%	106
Corn	Starch-g-poly-(N,N dimethyl acrylamide-co-acrylic acid)	With alteration, DS rose in it.	Cr(VI)	5.0	Langmuir	Pseudo second order	6.7	NR	107
Corm	Cross-linked amino starch	With a higher conversion ratio, the grafting percentage rose. temperature drop during gelatinization. A rise in the stability of heat.	Cr(VI)	7.0	NR	NR	28.8	NR	108
Patato	Porous starch xanthate	Degradation and solubilization occurred as the alkali concentration increased. Porosity decreases. The hydroxyl groups' hydrogen bonds disperse	Pb(II)	7.0	Langmuir	Pseudo second order	109	NR	109
NA	Hydroxyethyl starch-grafted-polyacrylamide	Protected crystalline structure.	Hg(II)	5.5	Langmuir	Pseudo second order	300.9	NR	110
Corn	Cross-linked starch grafted polyacrylamide	The cross-linked material showed an increase in both intrinsic viscosity and nitrogen concentration. The average molecular weight of viscosity also rose.	Cu(II)	6.0	Freundlich	Pseudo second order	878	80%	111
Corn	Dithiocarbamate modified glycidyl methacrylate strach	The starch exhibited an A-type XRD pattern. Diminished crystallinity.	Zn(II) Co(II) Cu(II) Ni(II) Cd(II)	5.5	Langmuir	Pseudo second order	13.4 13.6 20.3 10.8 28.2	NR	112

The interaction between metal ions and functional groups present on the surface of starch-based adsorbent is a crucial adsorption mechanism involved in the adsorption process of Cd^{2+}. The adsorption of Pb^{2+} can occur via complexation between oxygen-containing functional groups present in starch-based adsorbents and metal ions. Figure 7 illustrate the complexation between metal ions and oxygen-containing functional groups on the surface of starch-based adsorbent[115,116].

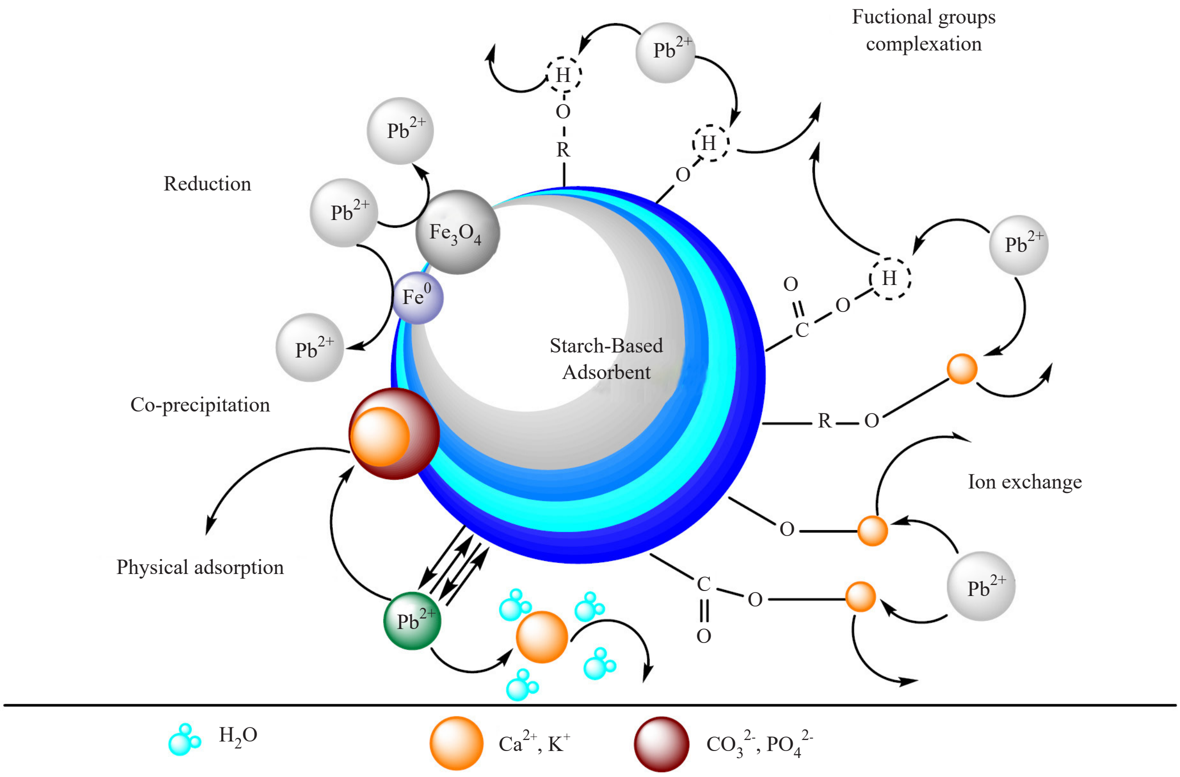


Figure 7. Illustrate the complexation between metal ions and oxygen-containing functional groups on the surface of Starch-Based Adsorbent

4. Starch based nanoparticles and composites for dye adsorption

To eliminate the cationic colour methyl violet from an aqueous solution, a mixture of clay, starch, and iron oxide was utilized. An average particle size of 179.6 nm was discovered for the composite, with a surface area of 74.27 m^2/g. 29.67 mg/g was the maximal sorption capacity of MV dye determined using the Langmuir method. This absorption quantity was found to be appropriate. At 25 °C, pH 9, and 150 minutes of contact time, the maximum MV dye removal effectiveness was 99.73 percent[117].

Free radicals are used in the creation of the magnetic Fe_3O_4@St-AcANCH starch-poly (acrylic acid) nanocomposite hydrogel, which is used to remove undesirable colour. On average, the Fe_2O_3 particles have a size of 70 nm. For CR and Fe_3O_4-St-AcANCH (0.2 g) per gram, the highest adsorption capacities of MV dyes are 99.32% and 97.5%, respectively[118].

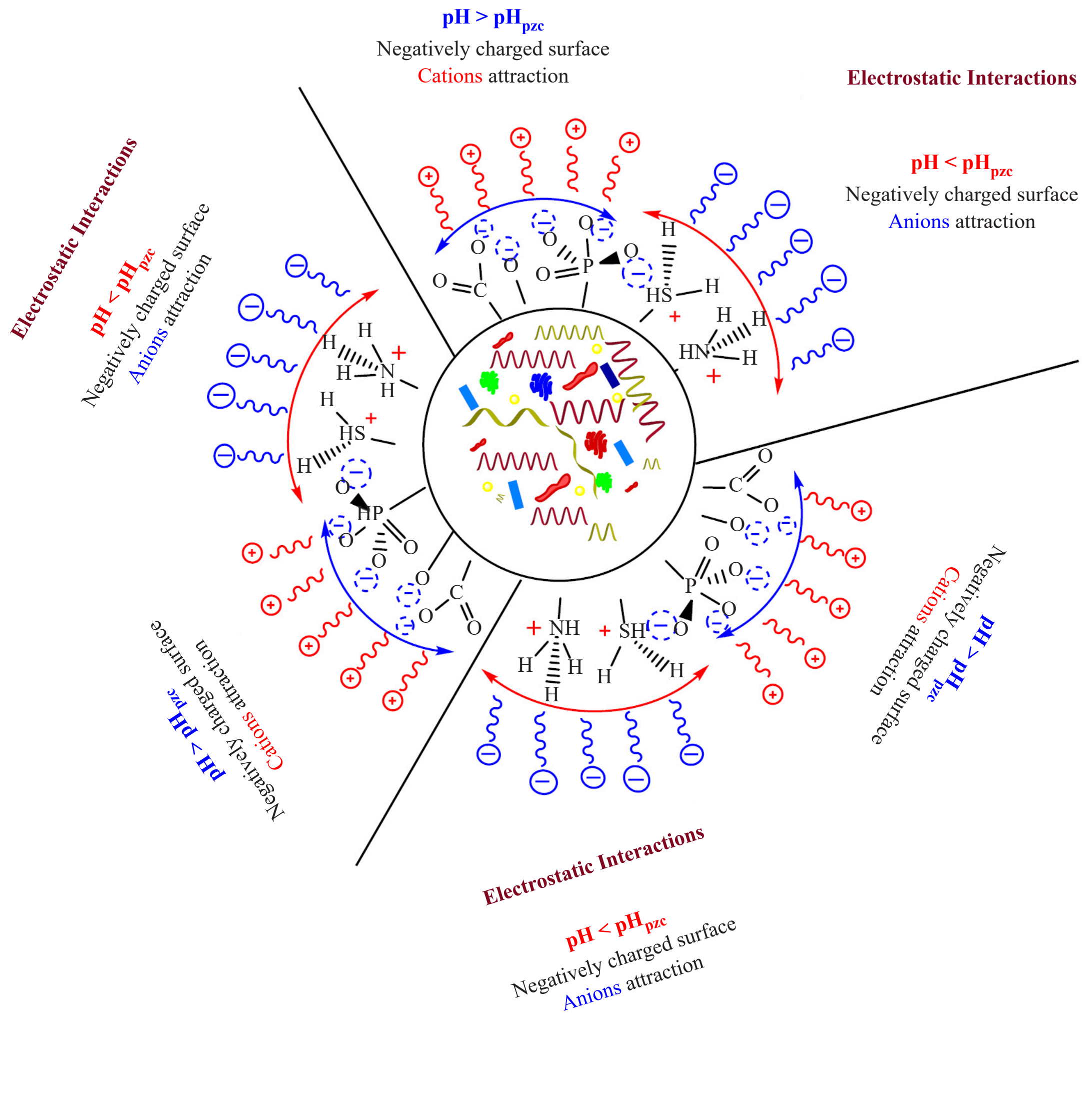
It seems possible to produce poly (acrylic acid) hydrogel efficiently when N, N-methylene bis-acrylamide and epichlorohydrin (ECH) are utilised as cross-linkers for starch. With adsorption maxima of 133.65 mg/g for the cationic dye (methylene blue) and 64.73 mg/g for the anionic dye (congo red), the mixed hydrogel with positive and negative charges showed amphoteric characteristics and was able to remove both types of dyes[40].

It was successfully developed and used to remove MB dye from the eggshell composite using polyamide grafting (CMP). Adsorption of 345 mg/g of MB dye at 298 K was achieved by the CMP. Electrostatic attraction, complex formation, interaction between π and π, and contact with functional groups were the mechanisms involved in adsorption[119], as shown in Figure 8.

Using the innovative magnetic nano-adsorbent nanoparticle@starch-g-poly(vinylsulphate)nanocomposite (MNP@St-g-PLVSs), the cationic dyes malachite green (MG) and methylene blue (MB) were recovered from waste water. With the MNP@St-g-PVS magnetic nano-adsorbent, cationic dye adsorption rates of 621 $mg \cdot g^{-1}$ for MB and 567 $mg \cdot g^{-1}$ for MG are readily achieved[6].

Starch-grafted copolymers of 2-acrylamido-2methyl propane sulfonate and acrylic acid (starch-co-AA) have been combined with a fraction of magnetite-functionalized cellulose nanocrystals (MCNCs) hydrogel to create bio-based nanocomposites. The adsorption capacities of the two cationic dyes were MV 2,500 mg/g and MB 428.6 mg/g, respectively, when they were introduced to the MCNCs-hydrogels[120].

After grafting polyacrylic acid (PAA) onto starch with success, the resultant starch-based hydrogel (STAH) was crosslinked N, N'-methylene-bisacrylamide (MBA) is employed. Additional COOH moreover COO groups increased the ability of STAH and MB to interact electrostatically, form hydrogen bonds, and engage in adsorption[121].



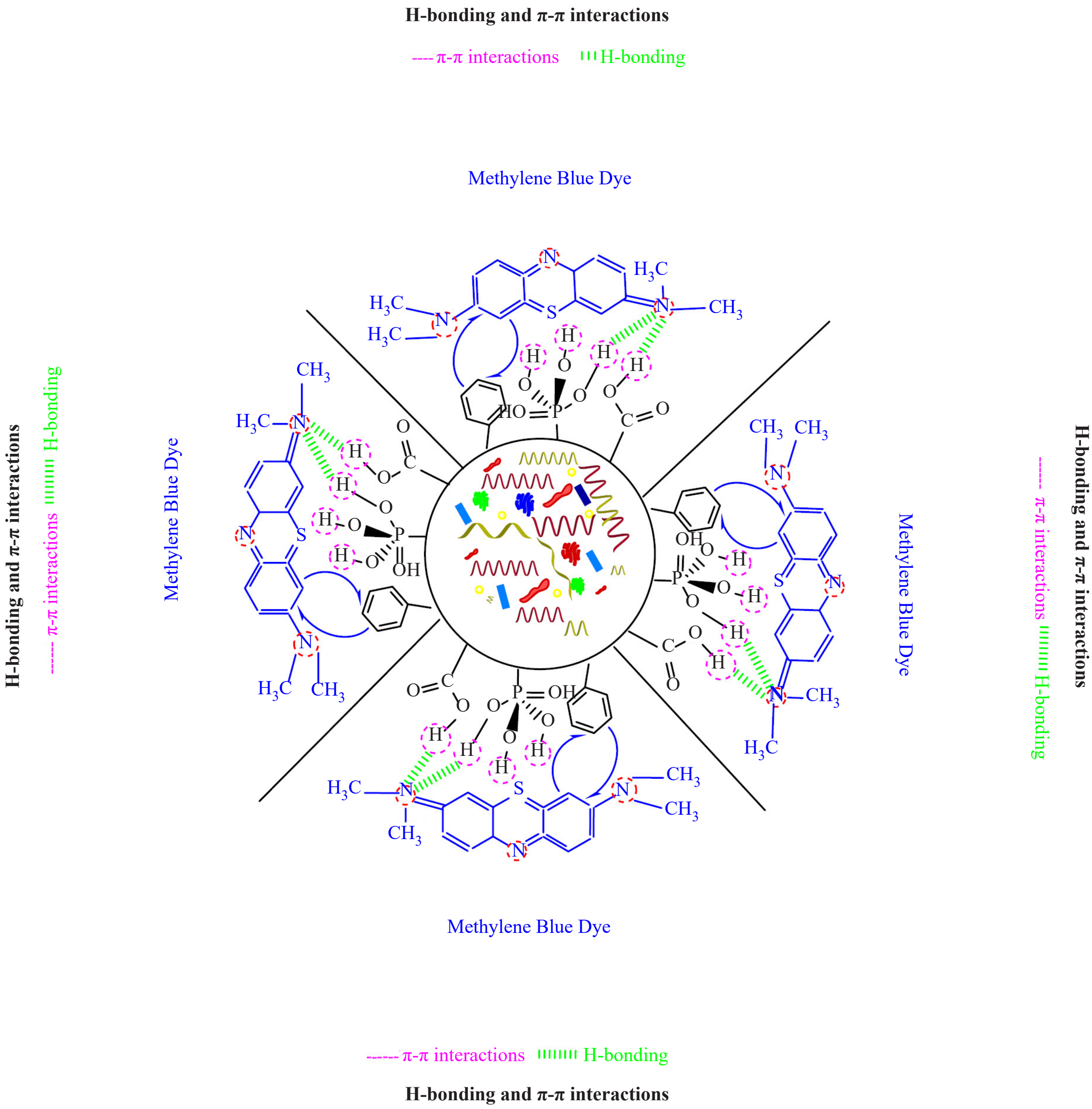


Figure 8. Electrostatic interactions-bonding and π-π interactions mechanisms[119]

Centered on the semi-IPN polymer network, a highly absorbent nanocomposite starch-graft poly(acrylicacid-co-acrylamide)/polyvinylalcohol/clinoptilolite(starch-g-p(AA-co-AAm)/PVA/clino) was created. A semi-IPN superabsorbent nanocomposite performed better than an average hydrogel, with a capacity of 364.82 g/g. There was an idea aquatic about them all[122].

Grafting poly(acrylic acid-co-acrylamide) with a free radical chemical to alter the starch backbone graft copolymerization technique resulted in the hydrogel composites $NiFe_2O_4$/SANCH and TiO_2/SANCH. The combined action of adsorption and photodegradation may eradicate CR dyes when $NiFe_2O_4$ and TiO_2 NPs, which possess a porous structure and increased thermal stability, are introduced[123].

5. Conclusion

In conclusion, the utilization of nano and macro adsorbents presents a promising avenue for the detoxification of synthetic dyes and heavy metals, contributing to sustainable starch strategies. These materials offer efficient removal of contaminants from wastewater, thereby addressing environmental concerns and promoting eco-friendly practices in various industries. Moving forward, future research directions could focus on enhancing the adsorption capacity, stability, and recyclability of these adsorbents. Additionally, exploring novel synthesis methods, investigating the potential synergistic effects of combined adsorbents, and assessing the feasibility of large-scale applications are crucial for advancing sustainable solutions in wastewater treatment. Furthermore, interdisciplinary collaborations between material scientists, environmental engineers, and chemists could lead to innovative approaches and the development of practical strategies for mitigating water pollution. Overall, continued efforts in this field hold significant promise for achieving sustainable development goals and safeguarding the environment for future generations. Enhanced Adsorption Performance Future research should aim to enhance the adsorption performance of nano and macro adsorbents. This could involve the exploration of novel materials with higher surface area, porosity, and functional groups tailored specifically for target contaminants. Additionally, optimizing process parameters such as pH, temperature, and contact time could improve adsorption efficiency. Stability and Recyclability Investigating the stability and recyclability of adsorbents is crucial for practical applications. Researchers can explore methods to enhance the stability of adsorbent materials under varying environmental conditions and evaluate their reusability through regeneration processes. Developing robust materials that maintain high adsorption capacity over multiple cycles will contribute to the sustainability of the detoxification process. Exploring synergistic effects through the combination of nano and macro adsorbents or hybrid materials could lead to enhanced performance compared to individual components. Future research could investigate the synergistic interactions between different adsorbents and optimize their compositions for synergistic effects. This approach may unlock new avenues for achieving higher adsorption efficiency and selectivity. Continuous exploration of innovative synthesis methods is essential for developing adsorbents with improved properties and performance. Researchers can explore green synthesis routes using sustainable precursors and eco-friendly processes to minimize environmental impact. Additionally, advancements in fabrication techniques such as sol-gel, hydrothermal, and microwave-assisted synthesis could lead to the production of tailored adsorbents with desirable characteristics. Transitioning laboratory-scale findings to large-scale applications require thorough techno-economic assessments. Future research should focus on evaluating the feasibility and cost-effectiveness of implementing nano and macro adsorbents in real-world wastewater treatment scenarios. Conducting life cycle assessments and considering factors such as scalability, operational costs, and regulatory compliance will be essential for successful implementation. Collaboration between multidisciplinary fields such as material science, environmental engineering, chemistry, and economics is essential for driving innovation in sustainable starch strategies. Interdisciplinary research teams can leverage diverse expertise to tackle complex challenges associated with water pollution and develop holistic solutions that balance environmental, economic, and social considerations. In summary, future research directions in the field of sustainable starch strategies should prioritize enhancing the adsorption performance, stability, and recyclability of nano and macro adsorbents. Exploring synergistic effects, optimizing synthesis methods, evaluating large-scale application feasibility, and fostering interdisciplinary collaborations will collectively contribute to advancing sustainable solutions for the detoxification of synthetic dyes and heavy metals in wastewater treatment. By addressing these research directions, we can pave the way toward a cleaner and more sustainable future for water resources and ecosystems.

Conflict of interest

The authors declare no competing financial interest.

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