


## Review

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

Wajeelha Naeem<sup>1</sup>, Fazal Haq<sup>1\*</sup>, Hashmat Ullah<sup>1</sup>, Abid Khan<sup>1</sup>, Rabia Kundi<sup>1</sup>, Irum Bukhari<sup>1</sup>, Iffat Ayesha Khan<sup>1</sup>, Mehwish Kiran<sup>2</sup>, Arshad Farid<sup>3</sup>

<sup>1</sup>Institute of Chemical Sciences, Gomal University, 29220 D.I.Khan, KPK, Pakistan

<sup>2</sup>Department of Horticulture Faculty of Agriculture, Gomal University, 29220 D.I.Khan, KPK, Pakistan

<sup>3</sup>Gomal Centre of Biochemistry and Biotechnology, Gomal University, 29220 D.I.Khan, KPK, Pakistan  
E-mail: drhaq@gu.edu.pk

**Received:** 15 March 2024; **Revised:** 23 May 2024; **Accepted:** 24 May 2024

**Abstract:** The research being conducted explores environmentally friendly techniques for the detoxification of heavy metals and synthetic dyes from aquariums using nano- and macro-adsorbents based on starch. In response to the urgent demand for sustainable wastewater treatment solutions, the research focuses on the development and evaluation of starch-based materials with enhanced adsorption capabilities. The effectiveness of macro- and nano-sized starch composites and starch-based adsorbents in facilitating the removal of heavy metals and synthetic dyes is evaluated. The review includes a thorough examination of equilibrium characteristics, kinetics, and adsorption mechanisms, and also considers how these sustainable starch-based products could be applied in real-world environmental remediation scenarios. The findings provide valuable insights into the development and implementation of starch-based adsorbents for the long-term, effective detoxification of heavy metals and synthetic dyes from water.

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

## 1. Introduction

Water contamination is typically caused by activities within the industrial sector<sup>1</sup>. The trash generated by industries such as food coloring, paper, plastic, textiles, leather tanning, and cosmetics<sup>2</sup> releases from 2 to 20% of dyes into wastewater<sup>3</sup>. The intricate aromatic structure of these synthetic pigments makes them resistant to heat, light, reducing agents, and biodegradation<sup>4</sup>. The chemicals that cause cancer and mutagenicity, their impact on human health, and their non-biodegradable nature on marine life<sup>5</sup>. 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<sup>6</sup>. 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<sup>7</sup>. Further, human activity and various industrial activities can contaminate the water bodies with heavy metals<sup>8</sup>. 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<sup>9</sup>. Anemia, nervous system disruption, liver and kidney damage, and anemia are only a few of the illnesses brought on by heavy metals<sup>10</sup>, tumors<sup>11</sup>, and dementia<sup>12</sup>. 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 oxidative metabolism<sup>13</sup>. These are the different issues causing by heavy metals in fish<sup>14</sup>. 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<sup>15</sup>. Because adsorbents are widely available, the adsorption process is straightforward, and the other ways are very effective, this is the most advantageous adsorption approach<sup>16</sup>. 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<sup>17</sup>. 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<sup>18</sup>. A recent estimate estimates the yearly worldwide production of dyes at over 70 lakh pounds<sup>19</sup>. 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<sup>20</sup>. It embraces metals as a consequence of fish species and other aquatic life becoming mutagenic or teratogenic<sup>21</sup>. 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<sup>22</sup>. As indicated by reports, dyes based on chromium often have a complex structure and can cause cancer in humans<sup>23</sup>. 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

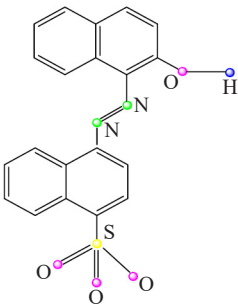
Types of dyes	An illustration of a dye's chemical composition	Dye examples	Employing dye	Water-soluble nature	Impacts of ecological toxicology	Ref.
Acid Dye	 <p>Acid Red 88</p>	Acid yellow 36 Acid orange 7 Acid blue 83	Industries: nylon, silk, and modified acrylics; textile, leather, and medicinal	solubility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

Table 1. (cont.)

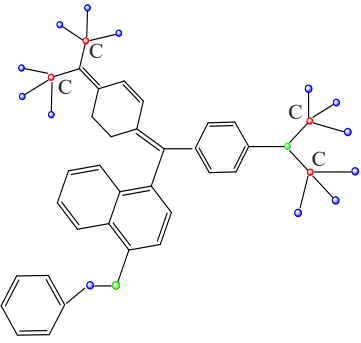
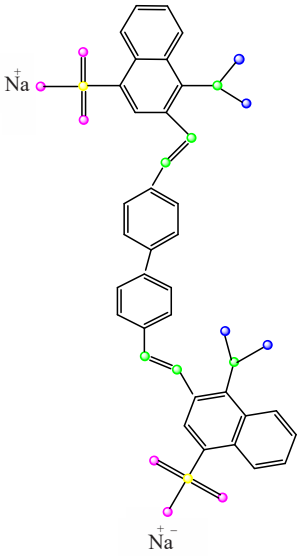
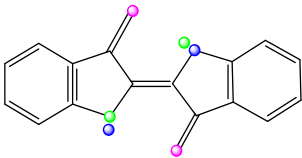
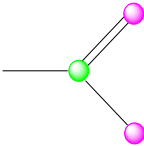
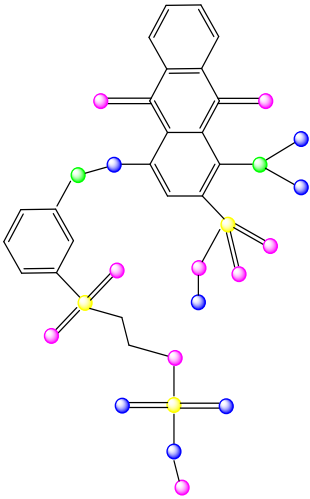
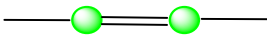
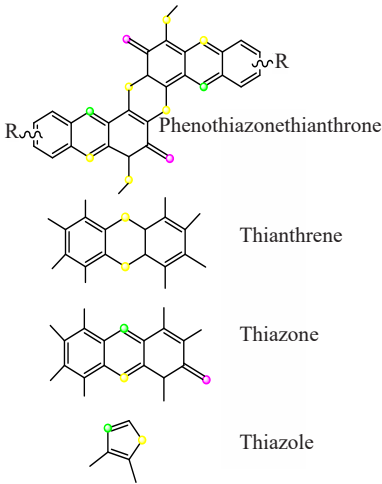
Types of dyes	An illustration of a dye's chemical composition	Dye examples	Employing dye	Water-soluble nature	Impacts of ecological toxicology	Ref.
Basic dye	 <p>Basic blue 26</p>	Methylene blue (MB), Basic red 1, or rhodamine 6G, Basic yellow 2	Nylons, modified polyesters, paper, and polyacrylonitrile modified	Soluble in water	inflicting harm to the flora and wildlife and changing the chemical and physical characteristics of aquatic environments	24
Direct dye	 <p>Direct red 28</p>	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	 <p>Vat blue 1</p>	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	 <p>Chromophore of nitro dye</p>	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

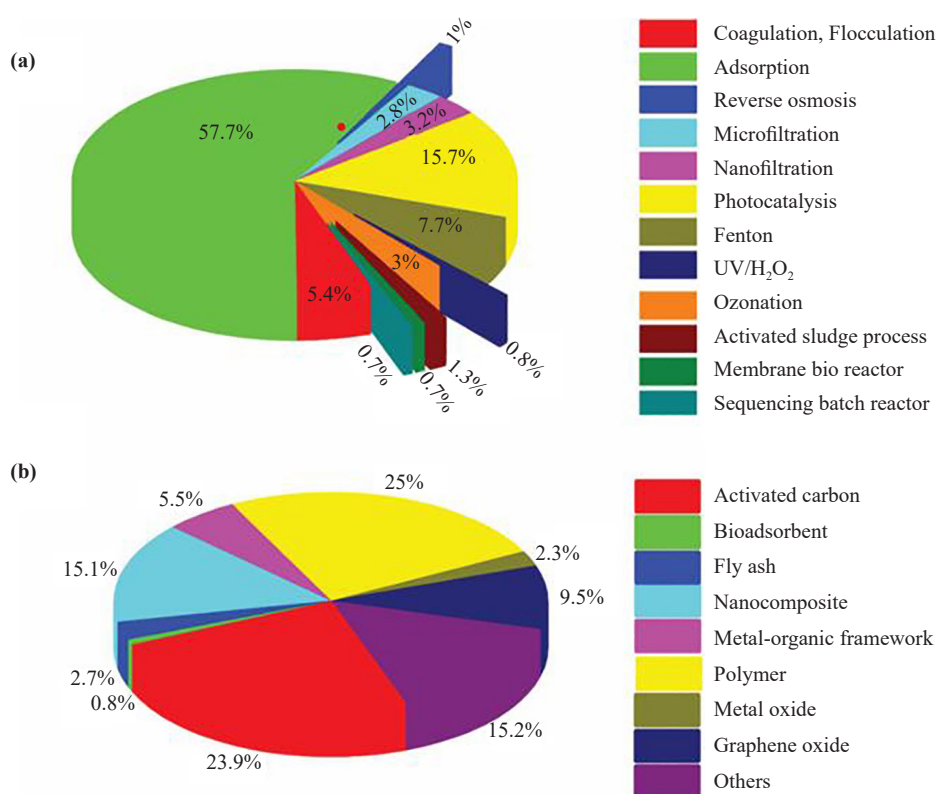
Table 1. (cont.)

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	 <p>Reactive blue 19</p>	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	 <p>Chromophore of Azo Dye</p>	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	 <p>Phenothiazonethianthrone</p> <p>Thianthrene</p> <p>Thiazone</p> <p>Thiazole</p>	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)<sup>29</sup>. Charged suspended and colloidal contaminants are destabilised during the coagulation process<sup>30</sup>. 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<sup>29</sup>. The emergence of solid hyperlinks between the dye molecules and the resins sets dye apart from wastewater<sup>31</sup>. 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<sub>2</sub>O<sub>2</sub>), and photocatalytic processes. A breakdown process that produces active oxygen pollutants (AOPs) occurs with certain pollutants<sup>32</sup>.

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<sup>33</sup>. Adsorption is a widely employed technique for extracting heavy metals, dyes, and arsenic, among other sorts of contaminants, from wastewater<sup>34</sup>. 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<sup>35</sup>. 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<sup>36</sup>.



**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 <sub>2</sub> O <sub>3</sub> 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 <sup>2</sup> /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.)

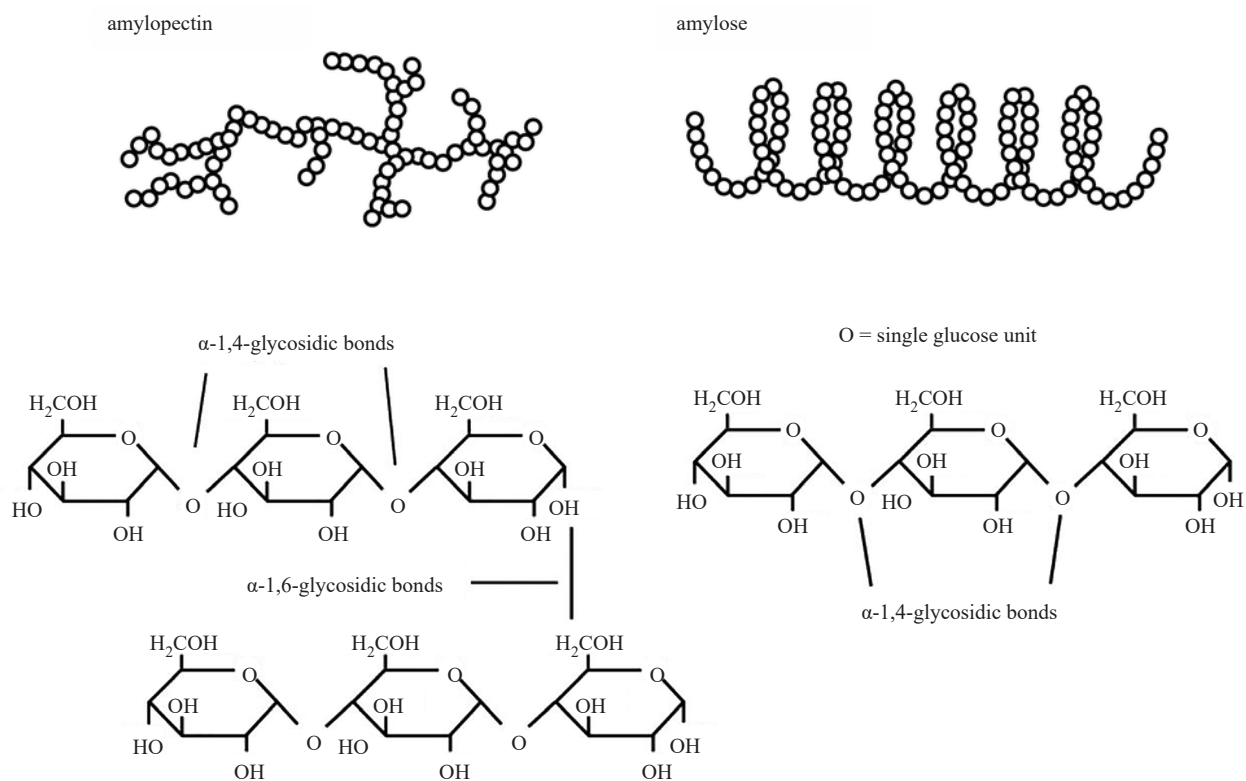
Adsorbent	Surface area (m <sup>2</sup> /g)	Dye	Adsorption conditions					Adsorption capacity (mg/g)	Isotherms/kinetics	Mechanism	Ref.
			pH	Time (min)	Conc. (mg/L)	Adsorbent dosage (g/L)	Temp (°C)				
Ethylenediamine Modified starch (CAS)	-	A010	4	1.5 h	800	0.05 g	25 ± 1	0.591	Langmuir/ PSO & PSO	Electrostatic 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<sub>6</sub>H<sub>10</sub>O<sub>5</sub>)<sup>56</sup>. 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<sup>57</sup>. 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-glucose units; amylopectin a branched chain polymer. In comparison, various varieties of rice contain varied quantities of amylopectin<sup>58</sup>. 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.

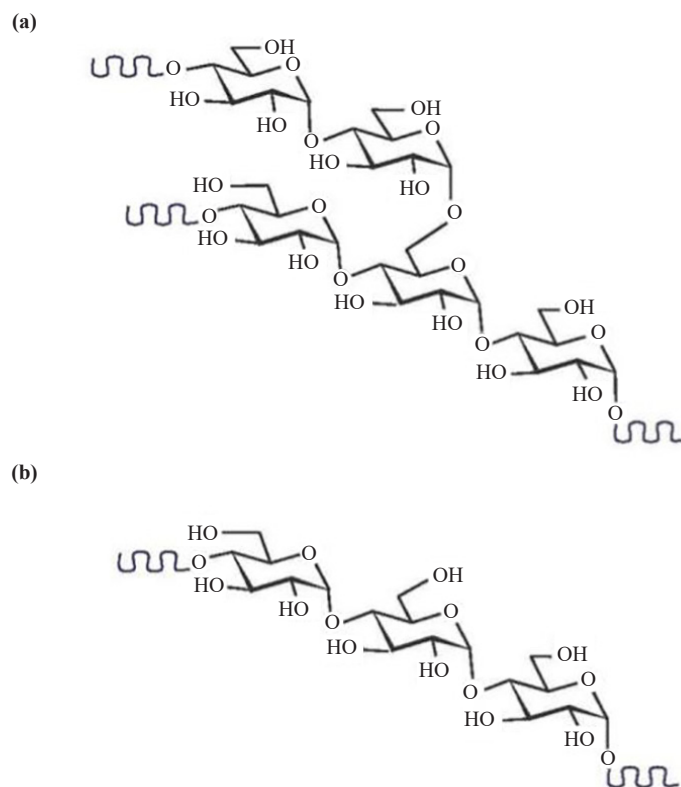
For green plants to retain energy for extended periods of time, they need granules generated from renewable starch. Densities of around 1.5 g/cm<sup>3</sup> have also been recorded for the semi-crystalline, closely packed starch granules. Using cryo-X-ray ptychographic tomography, a density of 1.36 g/cm 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<sup>59</sup>. 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<sup>60</sup>.

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<sup>61</sup>. 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<sup>62</sup>. Using data from the experiments, Figure 3 shows each stage of the starch granule’s hierarchical structure.

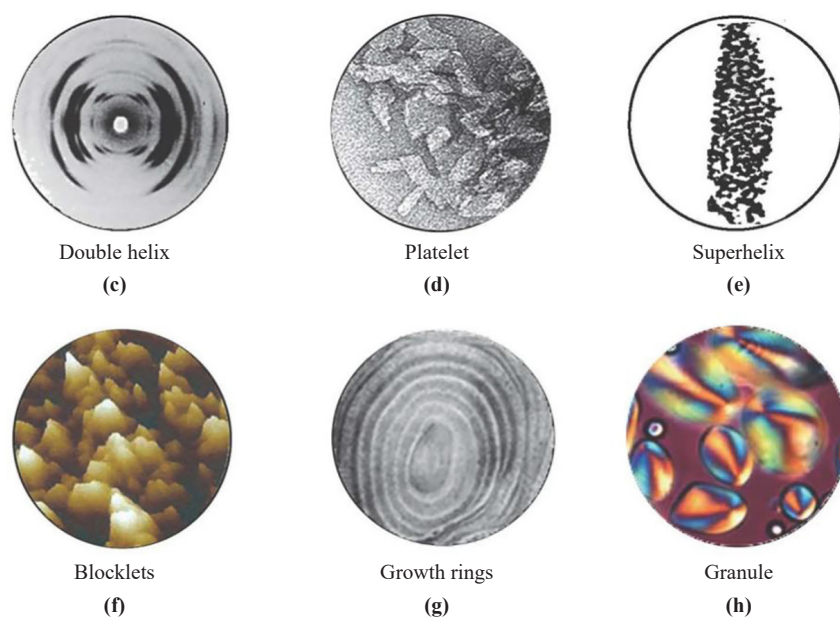




**Figure 2.** Structural composition of amylose and amylopectin







**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)<sup>59</sup>

The physicochemical traits observed in oxidized starches, such as decreased viscosity and heightened gelatinization enthalpy, illustrate how chemical alterations impact the properties of starch<sup>63</sup>. 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<sup>64</sup>. Methods for modifying starch, such as heat-moisture treatment and esterification, change its physicochemical characteristics, broadening its range of potential uses<sup>65</sup>. 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<sup>66a</sup>. 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<sup>66b</sup>.

### 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<sup>67</sup>. 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<sup>68</sup>. 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<sup>69</sup>. 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<sup>70</sup>. 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<sup>71</sup>. Figure 4 shows the oxidation mechanism of starch.

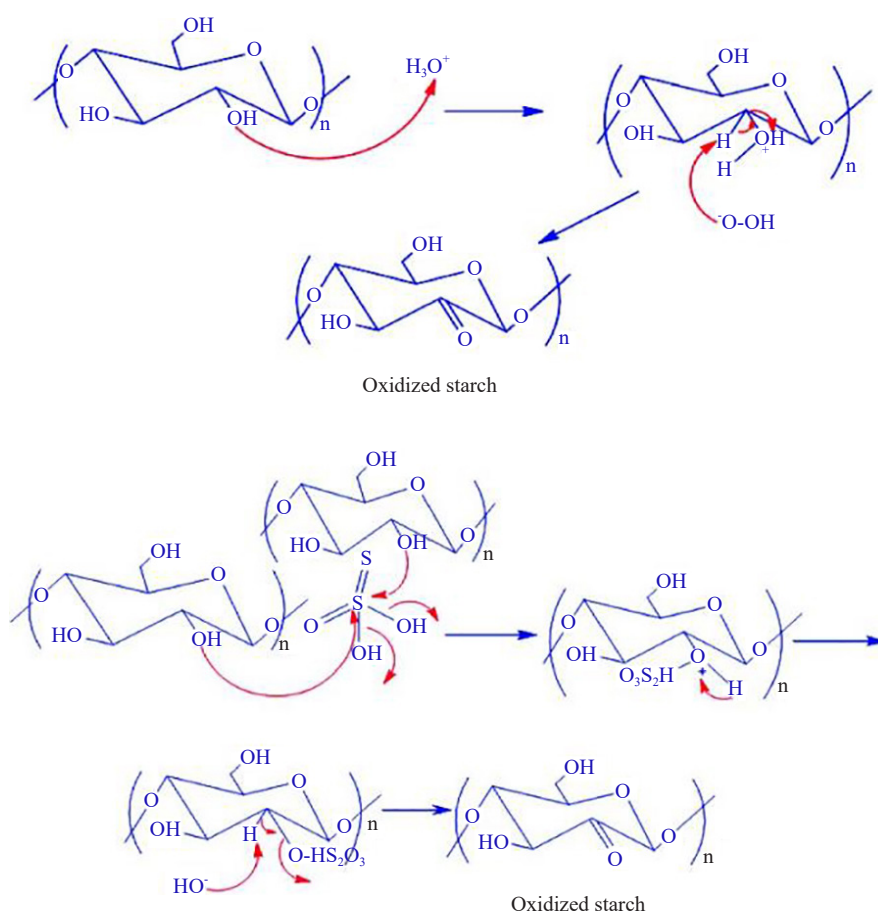


Figure 4. Oxidation mechanism of starch<sup>72</sup>

### 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<sup>6</sup>. Chemical linkages that join polymer chains to generate bridges between intermolecular hydrogen bonds are what create cross-linked starch<sup>73</sup>. 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<sup>74</sup>. The reactions of some of these reagents are depicted in the Figure 5 below.

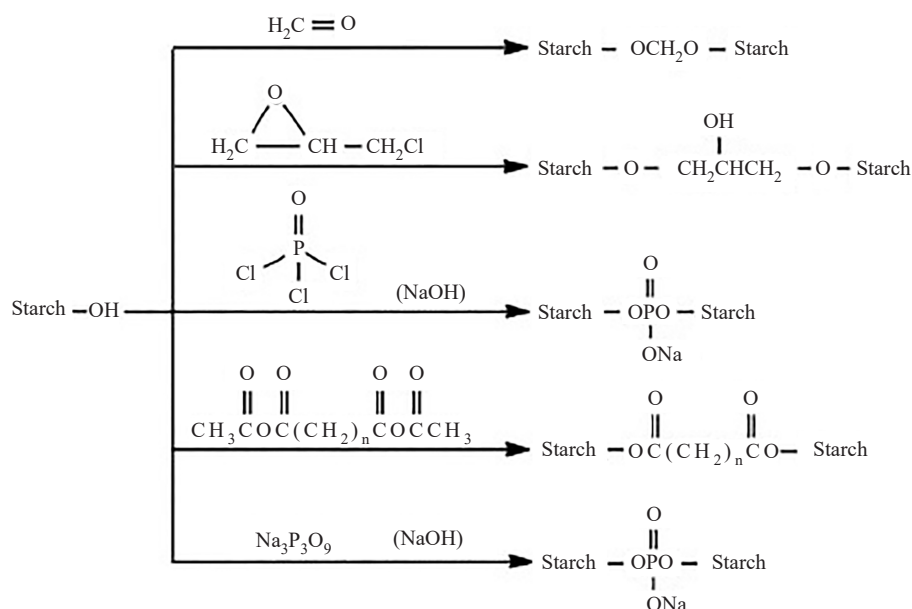


Figure 5. Cross-linking of starch<sup>6</sup>

### 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<sup>75</sup>. 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<sup>76</sup>. 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<sup>77</sup>. The synthesis of esterified starch is shown in Figure 6.

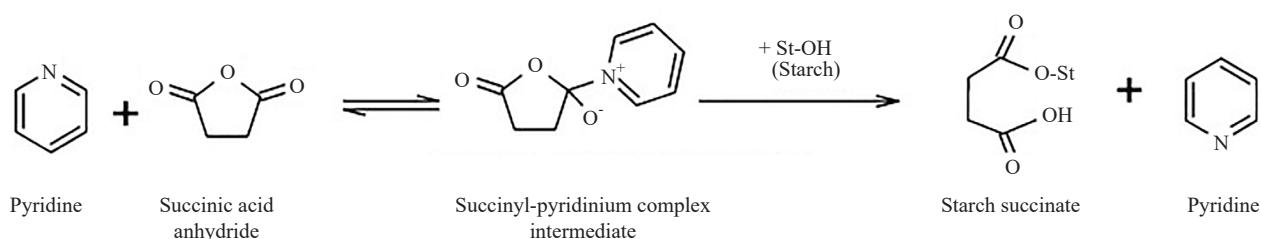


Figure 6. Synthesis of esterified starch

### 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<sup>78</sup>. 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<sup>79,80</sup>.

## 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<sup>81</sup>. 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<sup>82</sup>. 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<sup>83</sup>. 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<sup>84</sup>. 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<sup>85</sup>.

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<sup>86</sup>. Hydrothermal treatment represents a physical modification wherein the physicochemical properties of starch are altered without compromising the granular structure of the starch<sup>87</sup>. This transition occurs as the starch polymers shift from the amorphous to the semicrystalline region<sup>88</sup>. 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<sup>89</sup>.

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<sup>99</sup>. 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<sup>100</sup>.

## 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.

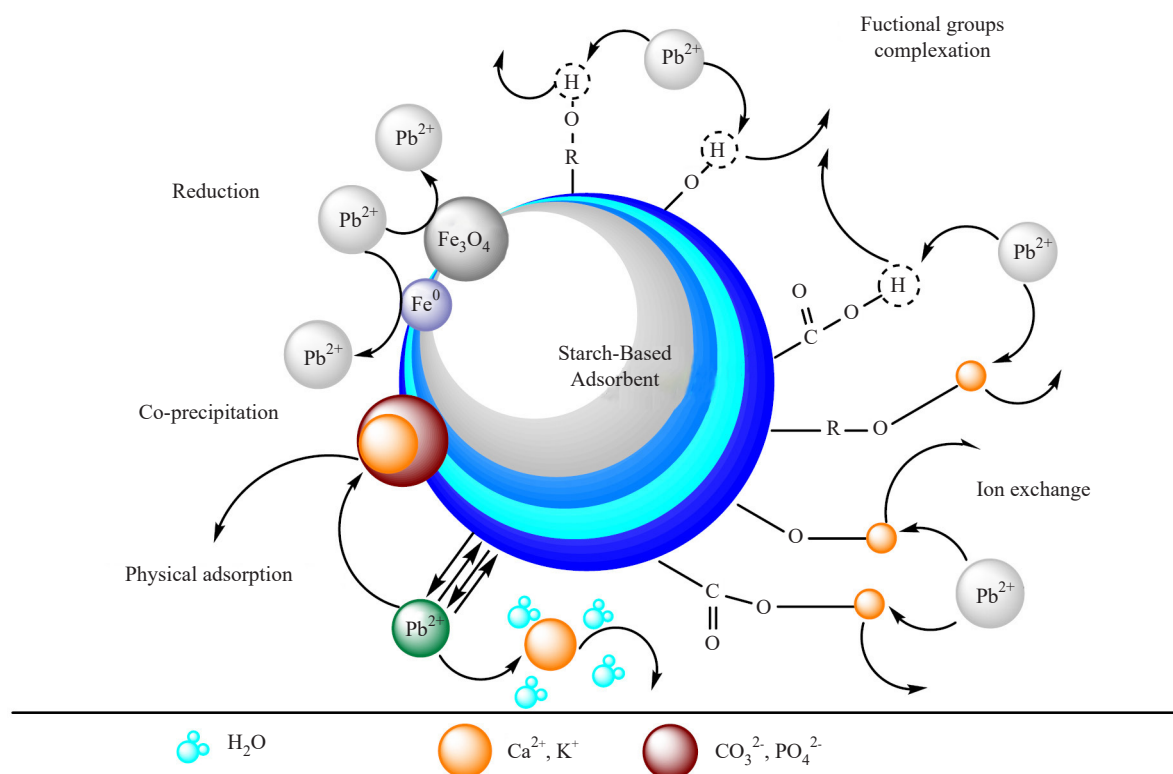
Starch-based binding agents have proven effective in immobilizing heavy metal ions, especially under alkaline conditions, showcasing starch's potential in sequestering heavy metal ions<sup>113</sup>. Moreover, exposing duckweed cultures to heavy metals has been demonstrated to hinder growth and trigger starch accumulation in a manner that correlates with the dosage, suggesting a direct link between heavy metal exposure and starch buildup<sup>114</sup>. 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 Hydrigel 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  $\text{Cd}^{2+}$ . The adsorption of  $\text{Pb}^{2+}$  can occur via complexation between oxygen-containing functional groups present in starch-based adsorbents and metal ions. Figure 7 illustrates the complexation between metal ions and oxygen-containing functional groups on the surface of starch-based adsorbent<sup>115,116</sup>.



**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<sup>2</sup>/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<sup>117</sup>.

Free radicals are used in the creation of the magnetic  $\text{Fe}_3\text{O}_4@\text{St-AcANCH}$  starch-poly (acrylic acid) nanocomposite hydrogel, which is used to remove undesirable colour. On average, the  $\text{Fe}_2\text{O}_3$  particles have a size of 70 nm. For CR and  $\text{Fe}_3\text{O}_4\text{-St-AcANCH}$  (0.2 g) per gram, the highest adsorption capacities of MV dyes are 99.32% and 97.5%, respectively<sup>118</sup>.

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<sup>40</sup>.

It was successfully developed and used to remove MB dye from the eggshell composite using polyamide

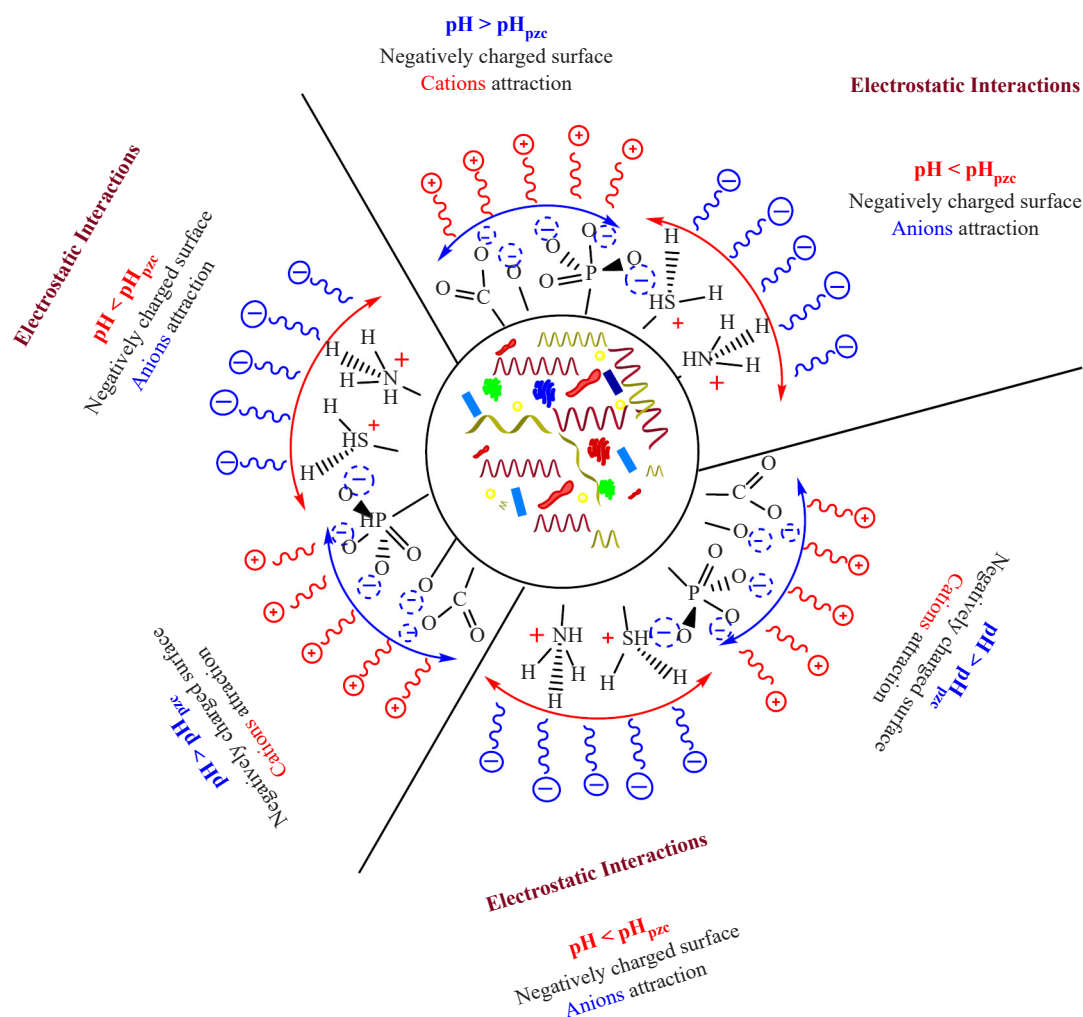


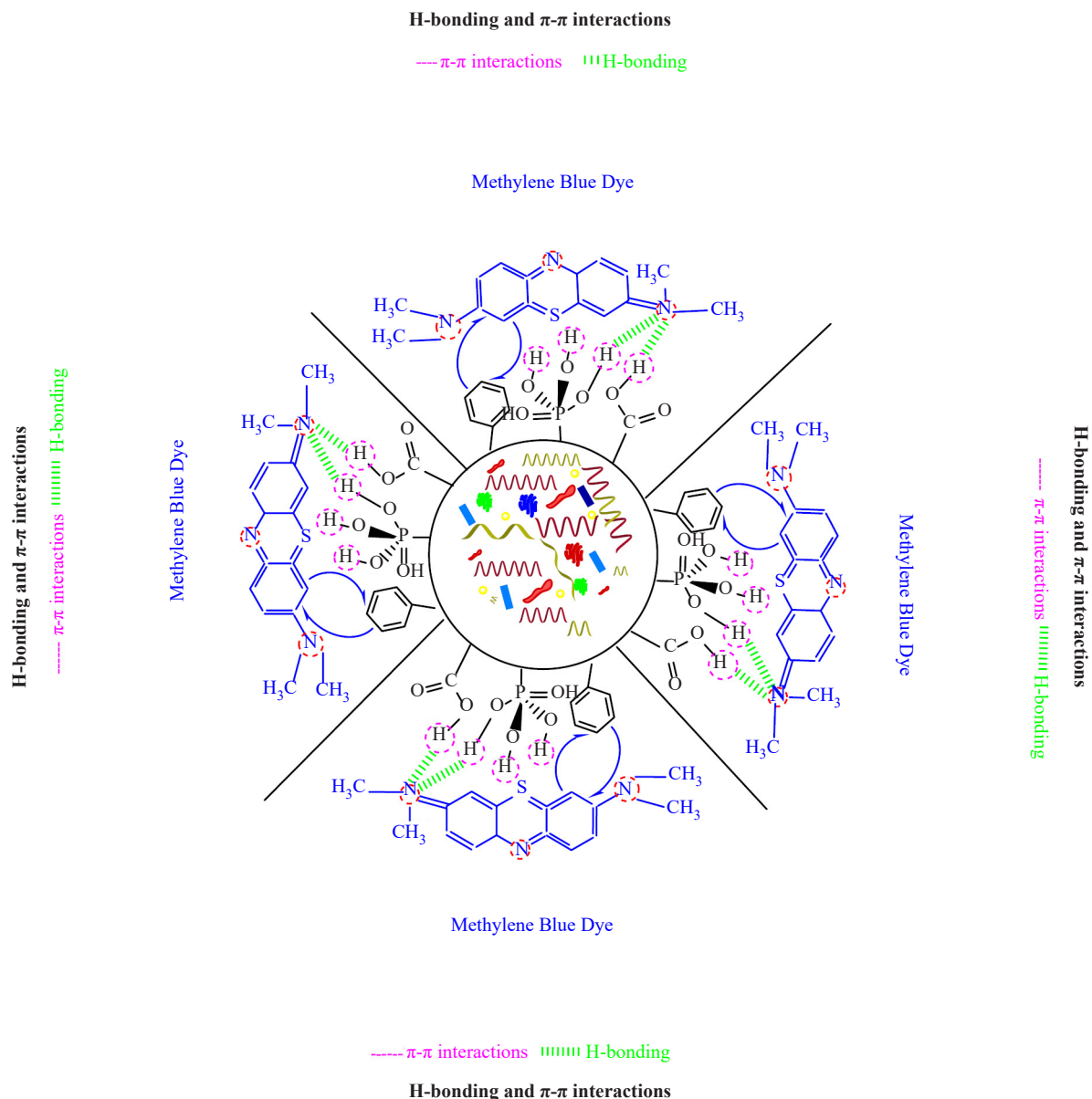
grafting (CMP). Adsorption of 345 mg/g of MB dye at 298 K was achieved by the CMP. Electrostatic attraction, complex formation, interaction between  $\pi$  and  $\pi$ , and contact with functional groups were the mechanisms involved in adsorption<sup>119</sup>, as shown in Figure 8.

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·g<sup>-1</sup> for MB and 567 mg·g<sup>-1</sup> for MG are readily achieved<sup>6</sup>.

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<sup>120</sup>.

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<sup>121</sup>.





**Figure 8.** Electrostatic interactions-bonding and  $\pi$ - $\pi$  interactions mechanisms<sup>119</sup>

Centered on the semi-IPN polymer network, a highly absorbent nanocomposite starch-graft poly(acrylic acid-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<sup>122</sup>.

Grafting poly(acrylic acid-co-acrylamide) with a free radical chemical to alter the starch backbone graft copolymerization technique resulted in the hydrogel composites  $\text{NiFe}_2\text{O}_4/\text{SANCH}$  and  $\text{TiO}_2/\text{SANCH}$ . The combined action of adsorption and photodegradation may eradicate CR dyes when  $\text{NiFe}_2\text{O}_4$  and  $\text{TiO}_2$  NPs, which possess a porous structure and increased thermal stability, are introduced<sup>123</sup>.

## 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.

## References

- [1] Pandey, S.; Do, J. Y.; Kim, J.; Kang, M. Fast and highly efficient removal of dye from aqueous solution using natural locust bean gum based hydrogels as adsorbent. *Int. J. Biol. Macromol.* **2020**, *143*, 60-75.

- [2] Ngwabebhoh, F. A.; Gazi, M.; Oladipo, A. A. Adsorptive removal of multi-azo dye from aqueous phase using a semi-IPN superabsorbent chitosan-starch hydrogel. *Chem. Eng. Res. and Des.* **2016**, *112*, 274-288.
- [3] Singh, R. P.; Singh, P. K.; Singh, R. L. Present status of biodegradation of textile dyes. *Curr Trends Biomed Eng Biosci.* **2017**, *3*(4), 555618.
- [4] Fosso-Kankeu, E.; Mittal, H.; Mishra, S. B.; Mishra, A. K. Gum ghatti and acrylic acid based biodegradable hydrogels for the effective adsorption of cationic dyes. *Ind. Eng. Chem. Res.* **2015**, *22*, 171-178.
- [5] Lei, C.; Pi, M.; Kuang, P.; Guo, Y.; Zhang, F. Organic dye removal from aqueous solutions by hierarchical calcined Ni-Fe layered double hydroxide, Isotherm, kinetic and mechanism studies. *J. Colloid Interface Sci.* **2017**, *496*, 158-166.
- [6] Haq, F.; Yu, H.; Wang, L.; Teng, L.; Haroon, M.; Khan, R. U.; Mehmood, S.; Ullah, R. S.; Khan, A.; Nazir, A. Advances in chemical modifications of starches and their applications. *Carbohydr. Res.* **2019**, *476*, 12-35.
- [7] Pohorille, A.; Pratt, L. R. Is water the universal solvent for life? *Orig. Life Evol. Biosph.* **2012**, *42*, 405-409.
- [8] Filippini, M.; Baldisserotto, A.; Menotta, S.; Fedrizzi, G.; Rubini, S.; Gigliotti, D.; Valpiani, G.; Buzzi, R.; Manfredini, S.; Vertuani, S. Heavy metals and potential risks in edible seaweed on the market in Italy. *Chemosphere* **2021**, *263*, 127983.
- [9] Bonanno, G.; Veneziano, V.; Orlando-Bonaca, M. Comparative assessment of trace element accumulation and biomonitoring in seaweed *Ulva lactuca* and seagrass *Posidonia oceanica*. *Sci. Total Environ.* **2020**, *718*, 137413.
- [10] Zhang, Y.; Wang, Y.; Zhang, H.; Li, Y.; Zhang, Z.; Zhang, W. Recycling spent lithium-ion battery as adsorbents to remove aqueous heavy metals, Adsorption kinetics, isotherms, and regeneration assessment. *Resour. Conserv. Recycl.* **2020**, *156*, 104688.
- [11] Altaf, M.; Yamin, N.; Muhammad, G.; Raza, M. A.; Shahid, M.; Ashraf, R. S. Electroanalytical techniques for the remediation of heavy metals from wastewater. *Water Pollution and Remediation, Heavy Metals.* **2021**, 471-511.
- [12] Li, M.; Messele, S. A.; Boluk, Y.; El-Din, M. G. Isolated cellulose nanofibers for Cu (II) and Zn (II) removal, performance and mechanisms. *Carbohydr. Polym.* **2019**, *221*, 231-241.
- [13] Sonone, S. S.; Jadhav, S.; Sankhla, M. S.; Kumar, R. Water contamination by heavy metals and their toxic effect on aquaculture and human health through food Chain. *Lett. Appl. NanoBioScience* **2020**, *10*(2), 2148-2166.
- [14] Khalfa, L.; Sdiri, A.; Bagane, M.; Cervera, M. L. A calcined clay fixed bed adsorption studies for the removal of heavy metals from aqueous solutions. *J. Clean. Prod.* **2021**, *278*, 123935.
- [15] Shahrokhi-Shahraki, R.; Benally, C.; El-Din, M. G.; Park, J. High efficiency removal of heavy metals using tire-derived activated carbon vs commercial activated carbon, Insights into the adsorption mechanisms. *Chemosphere* **2021**, *264*, 128455.
- [16] Ren, Z.; Jia, B.; Zhang, G.; Fu, X.; Wang, Z.; Wang, P.; Lv, L. Study on adsorption of ammonia nitrogen by iron-loaded activated carbon from low temperature wastewater. *Chemosphere* **2021**, *262*, 127895.
- [17] Lu, F.; Astruc, D. Nanocatalysts and other nanomaterials for water remediation from organic pollutants. *Coord. Chem. Rev.* **2020**, *408*, 213180.
- [18] Benkhaya, S.; M'rabet, S.; El Harfi, A. A review on classifications, recent synthesis and applications of textile dyes. *Inorg. Chem. Commun.* **2020**, *115*, 107891.
- [19] Ogugbue, C. J.; Sawidis, T. Bioremediation and detoxification of synthetic wastewater containing triarylmethane dyes by *Aeromonas hydrophila* isolated from industrial effluent. *Biotechnol. Res. Int.* **2011**, *2021*, 967925.
- [20] Nasar, A.; Mashkoor, F. Application of polyaniline-based adsorbents for dye removal from water and wastewater-a review. *Environ Sci Pollut Res.* **2019**, *26*, 5333-5356.
- [21] Deering, K.; Spiegel, E.; Quaisser, C.; Nowak, D.; Rakete, S.; Garí, M.; Bose-O'Reilly, S. Exposure assessment of toxic metals and organochlorine pesticides among employees of a natural history museum. *Environ. Res.* **2020**, *184*, 109271.
- [22] Lellis, B.; Fávaro-Polonio, C. Z.; Pamphile, J. A.; Polonio, J. C. Effects of textile dyes on health and the environment and bioremediation potential of living organisms. *BIORI.* **2019**, *3*(2), 275-290.
- [23] Yagub, M. T.; Sen, T. K.; Afroze, S.; Ang, H. M. Dye and its removal from aqueous solution by adsorption, a review. *Adv. Colloid Interface Sci.* **2014**, *209*, 172-184.
- [24] Madamwar, D.; Tiwari, O.; Jain, K. *Mapping of research outcome on remediation of dyes, dye intermediates and textile industrial waste: a research compendium*; New Delhi: Sardar Patel University Vallabh Vidyanagar, 2019.
- [25] Xiao, H.; Zhao, T.; Li, C.-H.; Li, M.-Y. Eco-friendly approaches for dyeing multiple type of fabrics with cationic reactive dyes. *J. Clean. Prod.* **2017**, *165*, 1499-1507.
- [26] Yamjala, K.; Nainar, M. S.; Ramiseti, N. R. Methods for the analysis of azo dyes employed in food industry-a review. *Food Chem.* **2016**, *192*, 813-824.
- [27] Gičević, A.; Hindija, L.; Karačić, A. Toxicity of azo dyes in pharmaceutical industry. In *CMBEBIH 2019*;

Badnjevic, A., Škrbić, R., Gurbeta Pokvić, L., Eds.; IFMBE Proceedings, vol 73. Springer, Cham., 2020; pp 581-587.

- [28] Berradi, M.; Hsissou, R.; Khudhair, M.; Assouag, M.; Cherkaoui, O.; El Bachiri, A.; El Harfi, A. Textile finishing dyes and their impact on aquatic environs. *Heliyon* **2019**, *5*(11), e02711.
- [29] Urbina-Suarez, N. A.; Barajas-Solano, A. F.; Zuurro, A.; Machuca, F. Advanced oxidation processes with uv-h<sub>2</sub>o<sub>2</sub> for nitrification and decolorization of dyehouse wastewater. *Chem. Eng. Trans.* **2022**, *95*, 235-240.
- [30] Gupta, B.; Priya, T.; Mishra, B. K. Augmentation of the coagulation activity of alum using a porous bio-flocculant for the remediation of trihalomethanes-generating hydrophobic natural organic matter. *Environ. Eng. Res.* **2021**, *26*(3), 200234.
- [31] Samsami, S.; Sarrafzadeh, M.-H.; Ahmadi, A. Surface modification of thin-film nanocomposite forward osmosis membrane with super-hydrophilic MIL-53 (Al) for doxycycline removal as an emerging contaminant and membrane antifouling property enhancement. *J. Chem. Eng.* **2022**, *431*, 133469.
- [32] Kuila, S. K.; Gorai, D. K.; Gupta, B.; Gupta, A. K.; Tiwary, C. S.; Kundu, T. K. Lanthanum ions decorated 2-dimensional g-C<sub>3</sub>N<sub>4</sub> for ciprofloxacin photodegradation. *Chemosphere* **2021**, *268*, 128780.
- [33] Tong, Y.; McNamara, P. J.; Mayer, B. K. Adsorption of organic micropollutants onto biochar, a review of relevant kinetics, mechanisms and equilibrium. *Environmental Science, Water Res.* **2019**, *5*(5), 821-838.
- [34] Awual, M. R. Novel conjugated hybrid material for efficient lead (II) capturing from contaminated wastewater. *Mater. Sci. Eng. C* **2019**, *101*, 686-695.
- [35] Thamer, B.; Aldalbahi, A. M. Moydeen A, H. El-Hamshary, AM Al-Enizi and MH El-Newehy. *Mater. Chem. Phys.* **2019**, *234*, 133-145.
- [36] Godiya, C. B.; Ruotolo, L. A. M.; Cai, W. Functional biobased hydrogels for the removal of aqueous hazardous pollutants, current status, challenges, and future perspectives. *J. Mater. Chem A* **2020**, *8*(41), 21585-21612.
- [37] Li, P.; Gao, B.; Li, A.; Yang, H. Evaluation of the selective adsorption of silica-sand/anionized-starch composite for removal of dyes and Copper (II) from their aqueous mixtures. *Int. J. Biol. Macromol* **2020**, *149*, 1285-1293.
- [38] Mokhtar, A.; Abdelkrim, S.; Zaoui, F.; Sassi, M.; Boukoussa, B. Improved stability of starch@layered-materials composite films for methylene blue dye adsorption in aqueous solution. *J. Inorg. Organomet. Polym. Mater.* **2020**, *30*(9), 3826-3831.
- [39] Farag, A. M.; Sokker, H. H.; Zayed, E. M.; Eldien, F. A. N.; Abd Alrahman, N. M. Removal of hazardous pollutants using bifunctional hydrogel obtained from modified starch by grafting copolymerization. *Int. J. Biol. Macromol* **2018**, *120*, 2188-2199.
- [40] Sarmah, D.; Karak, N. Double network hydrophobic starch based amphoteric hydrogel as an effective adsorbent for both cationic and anionic dyes. *Carbohydr. Polym.* **2020**, *242*, 116320.
- [41] Ilgin, P.; Ozay, H.; Ozay, O. The efficient removal of anionic and cationic dyes from aqueous media using hydroxyethyl starch-based hydrogels. *Cellulose* **2020**, *27*(8), 4787-4802.
- [42] Stan, M.; Lung, I.; Soran, M.-L.; Opris, O.; Leostean, C.; Popa, A.; Copaciu, F.; Lazar, M. D.; Kacso, I.; Silipas, T.-D. Starch-coated green synthesized magnetite nanoparticles for removal of textile dye optilan blue from aqueous media. *J. Taiwan Inst. Chem. Eng.* **2019**, *100*, 65-73.
- [43] Azeez, L.; Lateef, A.; Adejumo, A. L.; Adeleke, J. T.; Adetoro, R. O.; Mustapha, Z. Adsorption behaviour of rhodamine B on hen feather and corn starch functionalized with green synthesized silver nanoparticles (AgNPs) mediated with cocoa pods extracts. *CHEM AFR.* **2020**, *3*, 237-250.
- [44] Chen, Q. J.; Zheng, X. M.; Zhou, L. L.; Zhang, Y. F. Adsorption of Cu (II) and methylene blue by succinylated starch nanocrystals. *Starch-Stärke* **2019**, *71*(7-8), 1800266.
- [45] Alvarado, N.; Abarca, R. L.; Urdaneta, J.; Romero, J.; Galotto, M. J.; Guarda, A. Cassava starch, structural modification for development of a bio-adsorber for aqueous pollutants. Characterization and adsorption studies on methylene blue. *Polym. Bull.* **2021**, *78*, 1087-1107.
- [46] Haroon, M.; Wang, L.; Yu, H.; Ullah, R. S.; Khan, R. U.; Chen, Q.; Liu, J. Synthesis of carboxymethyl starch-g-polyvinylpyrrolidones and their properties for the adsorption of rhodamine 6G and ammonia. *Carbohydr. Polym.* **2018**, *186*, 150-158.
- [47] Xia, K.; Liu, X.; Wang, W.; Yang, X.; Zhang, X. Synthesis of modified starch/polyvinyl alcohol composite for treating textile wastewater. *Polym.* **2020**, *12*(2), 289.
- [48] Mahmoodi, N. M.; Roudaki, M. S. M. A.; Didehban, K.; Saeb, M. R. Ethylenediamine/glutaraldehyde-modified starch, A bioplatfrom for removal of anionic dyes from wastewater. *Korean J Chem Eng.* **2019**, *36*, 1421-1431.
- [49] Guo, J.; Wang, J.; Zheng, G.; Jiang, X. Optimization of the removal of reactive golden yellow SNE dye by cross-linked cationic starch and its adsorption properties. *J. Eng. Fibers Fabr.* **2019**, *14*, 1-13.
- [50] Sharifpour, E.; Ghaedi, M.; Asfaram, A.; Farsadrooh, M.; Dil, E. A.; Javadian, H. Modeling and optimization of



ultrasound-assisted high performance adsorption of Basic Fuchsin by starch-capped zinc selenide nanoparticles/AC as a novel composite using response surface methodology. *Int. J. Biol. Macromol* **2020**, *152*, 913-921.

- [51] Sadik, W. A.-A.; El-Demerdash, A.-G. M.; Abbas, R.; Gabre, H. A. Fast synthesis of an eco-friendly starch-grafted poly (N, N-dimethyl acrylamide) hydrogel for the removal of Acid Red 8 dye from aqueous solutions. *Polym. Bull.* **2020**, *77*, 4445-4468.
- [52] Bao, L.; Zhu, X.; Dai, H.; Tao, Y.; Zhou, X.; Liu, W.; Kong, Y. Synthesis of porous starch xerogels modified with mercaptosuccinic acid to remove hazardous gardenia yellow. *Int. J. Biol. Macromol* **2016**, *89*, 389-395.
- [53] Gao, P.; Chen, D.; Chen, W.; Sun, J.; Wang, G.; Zhou, L. Facile synthesis of amine-crosslinked starch as an efficient biosorbent for adsorptive removal of anionic organic pollutants from water. *Int. J. Biol. Macromol* **2021**, *191*, 1240-1248.
- [54] Cheng, R.; Ou, S.; Li, M.; Li, Y.; Xiang, B. Ethylenediamine modified starch as biosorbent for acid dyes. *J. Hazard. Mater* **2009**, *172*(2-3), 1665-1670.
- [55] Hu, H.; Lin, C.; Zhang, Y.; Cai, X.; Huang, Z.; Chen, C.; Qin, Y.; Liang, J. Preparation of a stable nanoscale manganese residue-derived FeS@starch-derived carbon composite for the adsorption of safranin T. *Nanomater.* **2019**, *9*(6), 839.
- [56] Srivastava, R. K.; Shetti, N. P.; Reddy, K. R.; Kwon, E. E.; Nadagouda, M. N.; Aminabhavi, T. M. Biomass utilization and production of biofuels from carbon neutral materials. *Environ Pollut.* **2021**, *276*, 116731.
- [57] Apriyanto, A.; Compart, J.; Fettke, J. A review of starch, a unique biopolymer-structure, metabolism and in planta modifications. *Plant Sci.* **2022**, *318*, 111223.
- [58] Govindaraju, I.; Sunder, M.; Chakraborty, I.; Mumbreakar, K. D.; Mal, S. S.; Mazumder, N. Investigation of physico-chemical properties of native and gamma irradiated starches. *Mater. Today Proc.* **2022**, *55*, 12-16.
- [59] Spinozzi, F.; Ferrero, C.; Perez, S. The architecture of starch blocklets follows phyllotaxic rules. *Sci. Rep.* **2020**, *10*(1), 20093.
- [60] Dereje, B. Composition, morphology and physicochemical properties of starches derived from indigenous Ethiopian tuber crops, a review. *Int. J. Biol. Macromol* **2021**, *187*, 911-921.
- [61] Wedamulla, N.; Wijesinghe, W. Application of polysaccharides in food technology, a review. *Trends Carbohydr Res.* **2021**, *13*(2), 35-49.
- [62] Dai, L.; Zhang, J.; Cheng, F. Effects of starches from different botanical sources and modification methods on physicochemical properties of starch-based edible films. *Int. J. Biol. Macromol* **2019**, *132*, 897-905.
- [63] Shi, R.; Tang, N.; Zhang, X.; Cheng, Y. Characterization of physicochemical properties of hypochlorite oxidized starches and their suitability for making starch noodles. *Starch-Stärke* **2022**, *75*(3-4), 2200212.
- [64] Punia, S.; Dhull, S. B.; Manzoor, M.; Chandak, A.; Esua, O. J. Functionality and applications of non-conventional starches from different sources. *Starch-Stärke* **2023**, *76*(1-2), 2300073.
- [65] Thakur, K.; Sharma, S.; Sharma, R. Morphological and functional properties of millet starches as influenced by different modification techniques, a review. *Starch-Stärke* **2022**, *75*(3-4), 2200184.
- [66] Haq, F.; Mehmood, S.; Haroon, M.; Kiran, M.; Waseem, K.; Aziz, T.; Farid, A. Role of starch based materials as a bio-sorbents for the removal of dyes and heavy metals from wastewater. *J. Environ. Polym. Degrad.* **2022**, *30*(5), 1730-1748. (a); Obadi, M.; Xu, B. Review on the physicochemical properties, modifications, and applications of starches and its common modified forms used in noodle products. *Food Hydrocoll.* **2021**, *112*, 106286. (b).
- [67] Chakraborty, I.; N, P.; Mal, S. S.; Paul, U. C.; Rahman, M. H.; Mazumder, N. An insight into the gelatinization properties influencing the modified starches used in food industry, a review. *Food Sci Biotechnol.* **2022**, *15*(6), 1195-1223.
- [68] Ramadan, M. F.; Sitohy, M. Z. Phosphorylated starches, preparation, properties, functionality, and techno-applications. *Starch-Stärke* **2020**, *72*(5-6), 1900302.
- [69] Pandiselvam, R.; Manikantan, M.; Divya, V.; Ashokkumar, C.; Kaavya, R.; Kothakota, A.; Ramesh, S. Ozone, an advanced oxidation technology for starch modification. *Ozone-Sci Eng.* **2019**, *41*(6), 491-507.
- [70] Dimri, S.; Aditi, Bist, Y.; Singh, S. Oxidation of starch. In *Starch, Advances in Modifications, Technologies and Applications*; Springer, 2023; pp 55-82.
- [71] Ozkan, C. K.; Ozgunay, H.; Akat, H. Possible use of corn starch as tanning agent in leather industry, controlled (gradual) degradation by H<sub>2</sub>O<sub>2</sub>. *Int. J. Biol. Macromol* **2019**, *122*, 610-618.
- [72] Adeniyi, A. G.; Saliu, O. D.; Ighalo, J. O.; Olosho, A. I.; Bankole, D. T.; Amusat, S. O.; Kelani, E. O. Effects of selected bleaching agents on the functional and structural properties of orange albedo starch-based bioplastics. *J. Polym. Eng.* **2020**, *40*(2), 120-128.
- [73] Wang, X.; Huang, L.; Zhang, C.; Deng, Y.; Xie, P.; Liu, L.; Cheng, J. Research advances in chemical modifications of starch for hydrophobicity and its applications, a review. *Carbohydr. Polym.* **2020**, *240*, 116292.

- [74] Subroto, E.; Indiarito, R.; Djali, M.; Rosyida, H. D. Production and application of crosslinking-modified starch as fat replacer, a review. *Int. J. Eng. Trends Technol.* **2020**, *68*(12), 26-30.
- [75] Otache, M.; Duru, R.; Achugasim, O.; Abayeh, O. Advances in the modification of starch via esterification for enhanced properties. *J. Environ. Polym. Degrad.* **2021**, *29*(5), 1365-1379.
- [76] Ruhul Amin, M.; Anannya, F. R.; Mahmud, M. A.; Raian, S. Esterification of starch in search of a biodegradable thermoplastic material. *J. Polym. Res.* **2020**, *27*(1), 3.
- [77] Punia, S.; Kumar, M.; Siroha, A. K.; Kennedy, J. F.; Dhull, S. B.; Whiteside, W. S. Pearl millet grain as an emerging source of starch, a review on its structure, physicochemical properties, functionalization, and industrial applications. *Carbohydr. Polym.* **2021**, *260*, 117776.
- [78] Kang, H.; Liu, R.; Huang, Y. Graft modification of cellulose, methods, properties and applications. *Polym.* **2015**, *70*, A1-A16.
- [79] Roy, D.; Semsarilar, M.; Guthrie, J. T.; Perrier, S. Cellulose modification by polymer grafting, a review. *Chem Soc Rev.* **2009**, *38*(7), 2046-2064.
- [80] Bhattacharya, A.; Misra, B. Grafting, a versatile means to modify polymers, techniques, factors and applications. *Prog. Polym. Sci.* **2004**, *29*(8), 767-814.
- [81] Nawaz, H.; Waheed, R.; Nawaz, M.; Shahwar, D. Physical and chemical modifications in starch structure and reactivity. *Chemical Properties of Starch* **2020**, *9*, 13-35.
- [82] Das, A.; Sit, N. Modification of taro starch and starch nanoparticles by various physical methods and their characterization. *Starch-Stärke* **2021**, *73*(5-6), 2000227.
- [83] Sinhmar, A.; Pathera, A. K.; Sharma, S.; Nehra, M.; Thory, R.; Nain, V. Impact of various modification methods on physicochemical and functional properties of starch, a review. *Starch-Stärke* **2023**, *75*(1-2), 2200117.
- [84] Amaraweera, S. M.; Gunathilake, C.; Gunawardene, O. H.; Fernando, N. M.; Wanninayaka, D. B.; Dassanayake, R. S.; Rajapaksha, S. M.; Manamperi, A.; Fernando, C. A.; Kulatunga, A. K. Development of starch-based materials using current modification techniques and their applications, a review. *Mol.* **2021**, *26*(22), 6880.
- [85] Diyana, Z.; Jumaidin, R.; Selamat, M. Z.; Ghazali, I.; Julmohammad, N.; Huda, N.; Ilyas, R. Physical properties of thermoplastic starch derived from natural resources and its blends, a review. *Polym.* **2021**, *13*(9), 1396.
- [86] Majzoobi, M.; Radi, M.; Farahnaky, A.; Jamalain, J.; Tongtang, T.; Mesbahi, G. Physicochemical properties of pre-gelatinized wheat starch produced by a twin drum drier. *JAST.* **2011**, *13*(2), 193-202.
- [87] Olu-Owolabi, B. I.; Afolabi, T. A.; Adebawale, K. O. Pasting, thermal, hydration, and functional properties of annealed and heat-moisture treated starch of sword bean (*Canavalia gladiata*). *Int. J. Food Prop.* **2011**, *14*(1), 157-174.
- [88] Ashogbon, A. O.; Akintayo, E. T. Recent trend in the physical and chemical modification of starches from different botanical sources, a review. *Starch-Stärke* **2014**, *66*(1-2), 41-57.
- [89] Steeneken, P. A.; Woortman, A. J. Superheated starch, A novel approach towards spreadable particle gels. *Food Hydrocoll* **2009**, *23*(2), 394-405.
- [90] Lewandowicz, G.; Soral-Śmietana, M. Starch modification by iterated syneresis. *Carbohydr. Polym.* **2004**, *56*(4), 403-413.
- [91] Lim, S. T.; Han, J. A.; Lim, H.; BeMiller, J. Modification of starch by dry heating with ionic gums. *Cereal Chem.* **2002**, *79*(5), 601-606.
- [92] Pukkahuta, C.; Shobsngob, S.; Varavinit, S. Effect of osmotic pressure on starch, New method of physical modification of starch. *Starch-Stärke* **2007**, *59*(2), 78-90.
- [93] Zarguili, I.; Maache-Rezzoug, Z.; Loisel, C.; Doublier, J.-L. Influence of DIC hydrothermal process conditions on the gelatinization properties of standard maize starch. *J. Food Eng.* **2006**, *77*(3), 454-461.
- [94] Maache-Rezzoug, Z.; Maugard, T.; Zarguili, I.; Bezzine, E.; El Marzouki, M.-N.; Loisel, C. Effect of instantaneous controlled pressure drop (DIC) on physicochemical properties of wheat, waxy and standard maize starches. *J. Cereal Sci.* **2009**, *49*(3), 346-353.
- [95] Huang, Z.-Q.; Lu, J.-P.; Li, X.-H.; Tong, Z.-F. Effect of mechanical activation on physico-chemical properties and structure of cassava starch. *Carbohydr. Polym.* **2007**, *68*(1), 128-135.
- [96] Che, L.-M.; Li, D.; Wang, L.-J.; Dong Chen, X.; Mao, Z.-H. Micronization and hydrophobic modification of cassava starch. *Int. J. Food Prop.* **2007**, *10*(3), 527-536.
- [97] Han, Z.; Zeng, X.-a.; Zhang, B.-s.; Yu, S.-j. Effects of pulsed electric fields (PEF) treatment on the properties of corn starch. *J. Food Eng.* **2009**, *93*(3), 318-323.
- [98] Nemtanu, M. R.; Minea, R. *Functional properties of corn starch treated with corona electrical discharges*, *Macromol. Symp*; Wiley Online Library, 2006; pp 525-528.
- [99] Bangar, S. P.; Ashogbon, A. O.; Singh, A.; Chaudhary, V.; Whiteside, W. S. Enzymatic modification of starch, A



- green approach for starch applications. *Carbohydr. Polym.* **2022**, *287*, 119265.
- [100] Punia, S. Barley starch modifications, physical, chemical and enzymatic-a review. *Int. J. Biol. Macromol* **2020**, *144*, 578-585.
- [101] Bahrami, M.; Amiri, M. J.; Bagheri, F. Optimization of the lead removal from aqueous solution using two starch based adsorbents, Design of experiments using response surface methodology (RSM). *J. Environ. Chem. Eng.* **2019**, *7*(1), 102793.
- [102] Ibrahim, B. M.; Fakhre, N. A. Crown ether modification of starch for adsorption of heavy metals from synthetic wastewater. *Int. J. Biol. Macromol* **2019**, *123*, 70-80.
- [103] Qiao, D.; Li, S.; Yu, L.; Zhang, B.; Simon, G.; Jiang, F. Effect of alkanol surface grafting on the hydrophobicity of starch-based films. *Int. J. Biol. Macromol* **2018**, *112*, 761-766.
- [104] Liu, Q.; Li, F.; Lu, H.; Li, M.; Liu, J.; Zhang, S.; Sun, Q.; Xiong, L. Enhanced dispersion stability and heavy metal ion adsorption capability of oxidized starch nanoparticles. *Food Chem.* **2018**, *242*, 256-263.
- [105] Irani, M.; Ismail, H.; Ahmad, Z.; Fan, M. Synthesis of linear low-density polyethylene-g-poly (acrylic acid)-co-starch/organo-montmorillonite hydrogel composite as an adsorbent for removal of Pb (II) from aqueous solutions. *J. Environ. Sci.* **2015**, *27*, 9-20.
- [106] Mosafari, M.; Nemati, S.; Khataee, A.; Nasser, S.; Hashemi, A. A. Removal of Arsenic (III, V) from aqueous solution by nanoscale zero-valent iron stabilized with starch and carboxymethyl cellulose. *J. Environ. Health Sci.* **2014**, *12*, 1-11.
- [107] Kolya, H.; Roy, A.; Tripathy, T. Starch-g-Poly-(N, N-dimethyl acrylamide-co-acrylic acid), an efficient Cr (VI) ion binder. *Int. J. Biol. Macromol* **2015**, *72*, 560-568.
- [108] Hu, J.; Tian, T.; Xiao, Z. Preparation of cross-linked porous starch and its adsorption for chromium (VI) in tannery wastewater. *Polym. Adv. Technol.* **2015**, *26*(10), 1259-1266.
- [109] Ma, X.; Liu, X.; Anderson, D. P.; Chang, P. R. Modification of porous starch for the adsorption of heavy metal ions from aqueous solution. *Food Chem.* **2015**, *181*, 133-139.
- [110] Kolya, H.; Das, S.; Tripathy, T. Synthesis of Starch-g-Poly-(N-methylacrylamide-co-acrylic acid) and its application for the removal of mercury (II) from aqueous solution by adsorption. *Eur. Polym. J.* **2014**, *58*, 1-10.
- [111] Tan, J.; Wei, X.; Ouyang, Y.; Fan, J.; Liu, R. Adsorption properties of copper (II) ion from aqueous solution by starch-grafted polyacrylamide and crosslinked starch-grafted polyacrylamide. *Period. Polytech. Chem. Eng.* **2014**, *58*(2), 131-139.
- [112] Cheng, X.; Cheng, R.; Ou, S.; Li, Y. Synthesis and adsorption performance of dithiocarbamate-modified glycidyl methacrylate starch. *Carbohydr. Polym.* **2013**, *96*(1), 320-325.
- [113] Lappalainen, K.; Kärkkäinen, J.; Rusanen, A.; Wik, T. R.; Niemelä, M.; Madariaga, A. G.; Komulainen, S.; Keiski, R. L.; Lajunen, M. Binding of some heavy metal ions in aqueous solution with cationized or sulphonylated starch or waste starch. *Starch-Stärke* **2016**, *68*(9-10), 900-908.
- [114] Appenroth, K.-J.; Ziegler, P.; Sree, K. S. Accumulation of starch in duckweeds (Lemnaceae), potential energy plants. *Physiol Mol Biol Plants* **2021**, *27*(11), 2621-2633.
- [115] Wu, J.; Wang, T.; Zhang, Y.; Pan, W.-P. The distribution of Pb (II)/Cd (II) adsorption mechanisms on biochars from aqueous solution, Considering the increased oxygen functional groups by HCl treatment. *Bioresour. Technol.* **2019**, *291*, 121859.
- [116] Kołodziej, D.; Bąk, J. Use of three types of magnetic biochar in the removal of copper (II) ions from wastewaters. *Sep. Sci. Technol.* **2018**, *53*(7), 1045-1057.
- [117] Ansari Mojarad, A.; Tamjidi, S.; Esmacili, H. Clay/starch/Fe<sub>3</sub>O<sub>4</sub> nanocomposite as an efficient adsorbent for the removal of methyl violet dye from aqueous media. *J. Environ. Anal. Chem.* **2022**, *102*(19), 8159-8180.
- [118] Rahdar, S.; Rahdar, A.; Zafar, M. N.; Shafqat, S. S.; Ahmadi, S. Synthesis and characterization of MgO supported Fe-Co-Mn nanoparticles with exceptionally high adsorption capacity for Rhodamine B dye. *J. Mater. Res. Technol.* **2019**, *8*(5), 3800-3810.
- [119] Bin-Dahman, O. A.; Saleh, T. A. Synthesis of polyamide grafted on biosupport as polymeric adsorbents for the removal of dye and metal ions. *Biomass Convers. Biorefin.* **2024**, *14*(2), 2439-2452.
- [120] Moharrami, P.; Motamedi, E. Application of cellulose nanocrystals prepared from agricultural wastes for synthesis of starch-based hydrogel nanocomposites, efficient and selective nanoadsorbent for removal of cationic dyes from water. *Bioresour. Technol.* **2020**, *313*, 123661.
- [121] Chen, L.; Zhu, Y.; Cui, Y.; Dai, R.; Shan, Z.; Chen, H. Fabrication of starch-based high-performance adsorptive hydrogels using a novel effective pretreatment and adsorption for cationic methylene blue dye, behavior and mechanism. *J. Chem. Eng.* **2021**, *405*, 126953.
- [122] Olad, A.; Doustdar, F.; Gharekhani, H. Starch-based semi-IPN hydrogel nanocomposite integrated with

- clinoptilolite, preparation and swelling kinetic study. *Carbohydr. Polym.* **2018**, *200*, 516-528.
- [123]El-saied, H. A.-a.; El-Fawal, E. M. Green superabsorbent nanocomposite hydrogels for high-efficiency adsorption and photo-degradation/reduction of toxic pollutants from waste water. *Polym. Test.* **2021**, *97*, 107134.
- [124]Szymońska, J.; Krok, F.; Komorowska-Czepirska, E.; Rębilas, K., Modification of granular potato starch by multiple deep-freezing and thawing. *Carbohydr. Polym* **2003**, *52*(1), 1-10.