

# **Adsorption of Heavy Metals from Wastewater by Starch, Cellulose, Chitin, Chitosan and Lignin Biological Macro Molecule: Review Article**

# **Atıksulardan Ağır Metallerin Nişasta, Selüloz, Kitin, Kitosan ve Lignin Biyolojik Makro Molekül Tarafından Adsorpsiyonu: Derleme Makale**

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### **ABSTRACT**

 $\textbf{Contininant removal from sewage is a serious difficulty on the subject of water contamination. Association is a direct and  
Deficient technique for eliminating contaminants that involves the use of solid materials known as adsorbents. Mineral,$ organic, or biological adsorbent materials can be utilized. At the industrial scale, activated carbon is the favored traditional material. Activated carbon is widely used to remove contaminants from wastewater streams and to absorb them from groundwater, rivers, lakes, and reservoirs, which are all sources of potable water. However, because of its expensive cost, activated carbon is not widely used. Several ways of utilizing non-conventional adsorbents have been investigated over the last three decades to generate cheaper and more effective adsorbents to remove contaminants at trace levels. This article provides an overview of liquid-solid adsorption techniques for pollution removal that use low-cost polymer adsorbents. The paper discusses the fundamentals of adsorption and provides a classification for adsorbent materials as well as numerous low-cost biological macromolecule adsorbents, includes cellulose, starch, chitin, chitosan, lignin, and their heavy metal removal capability.

#### **Key Words**

Heavy metal ions, adsorption, biological macromolecule.

**Ö Z**

Kanalizasyondan kirleticilerin uzaklaştırılması, su kirliliği konusunda ciddi bir zorluktur. Adsorpsiyon, adsorban olarak bi-<br>Kinen katı maddelerin kullanımını içeren kirleticileri ortadan kaldırmak için doğrudan ve etkili ganik veya biyolojik adsorban maddeler kullanılabilir. Endüstriyel ölçekte, aktif karbon tercih edilen geleneksel malzemedir. Aktif karbon, atık su akışlarından kirleticileri uzaklaştırmak ve bunları yeraltı suyu, nehirler, göller ve rezervuarlardan emmek için yaygın olarak kullanılır; bunların hepsi içilebilir su kaynaklarıdır. Ancak, pahalı maliyeti nedeniyle aktif karbon yaygın olarak kullanılmamaktadır. Son otuz yılda, eser seviyelerde kirleticileri gidermek için daha ucuz ve daha etkili adsorbanlar üretmek amacıyla geleneksel olmayan adsorbanları kullanmanın çeşitli yolları araştırılmıştır. Bu makale, düşük maliyetli polimer adsorbanlar kullanan kirliliğin giderilmesi için sıvı-katı adsorpsiyon tekniklerine genel bir bakış sunmaktadır. Makalede adsorpsiyonun temelleri tartışılmakta ve adsorban malzemeler için bir sınıflandırma sağlanmakta ve ayrıca selüloz, nişasta, kitin, kitosan, lignin ve bunların ağır metal giderme kabiliyetleri de dahil olmak üzere çok sayıda düşük maliyetli biyolojik makromolekül adsorban sağlanmaktadır.

#### **Key Words**

Ağır metal iyonları, adsorpsiyon, biyolojik makromolekül.

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### **INTRODUCTION**

dsorption is the process where a gas or liquid solution forms a molecular or atomic layer on the surface of a solid or liquid (Fig. 1). The adsorbate or solute is the material that is adsorbed, and the adsorbent is the adsorbing phase. C.W. Anderson was the first to invent the term "adsorption." Scheele in 1773 for carbon-exposed gas. Lowitz noted the elimination of wood charcoal adds color and odor to water in 1785. The same was seen by Larvitz in 1792 and Kehl in 1793 with both vegetable and animal charcoals. Kayser, on the other hand, was the first to use the term adsorption to difference exterior collection from intermolecular penetration, in 1881. He proposed that the chief property of adhesion is material exterior cumulation. Activated carbon was originally employed for municipal water remedy in the 1940s and 1950s, but the technology was not generally adopted until then [1].

Physical adsorption occurs when the attraction among the solid layer and the adsorbed particles is physical in character, the attractive forces are weak Van der Waals forces, and the resultant adsorption is reversible in nature. The adsorption process is called Chemisorption when a strong chemical bond is formed between linked particles and the solid phase, and it is hard to eliminate chemisorbed particles from the solid phase [2].

Solvent adsorption is influenced by both physical and chemical forces. Vandervals and electrostatic forces are examples of physical forces. The chemical forces are the product of a fast inter-union rate including the development of inner substances like a process for a bond exchange and symbiotic links, as well as hydrogen bonds [3]. Adsorption can be split into two sorts based on this: The first is natural adsorption, also known as Vander Waals adsorption, which is a natural interaction among the surface of an atom, species, or ions which adsorb on it. Physisorption is non-distinct because the molecule that is affected by it is not chemically bonded to the atoms' surface, but rather presents a specific surface area [4]. The size of the atoms, particles, or volatised ions determines the occupied area, and the physisorption heat is low. Physical adsorption does not need reactive energy, that is a reverse operation [5], and the process of adsorption happens when a surface allows the movement of atoms, molecules, or ions within a defined region, preventing them from being nonlocalized. The process of this type of adsorption involves many surface layers

as well. Chemical adsorption, also known as chemisorption, is the second type. This type of hydrogen bond is created among the surface and the atoms, particles, or ions that adsorb on it. Chemisorption is distinguished by its secrecy (distinct) Adsorption may or may not take place on the other surface under identical circumstances or on the surfac<<Eqn014.eps>>e itself while the neighboring conditions change Chemical adsorption. Larger heat output than that released by physisorption, the heat released while typical chemical bonds are formed may be reached. Energizing energy is required for chemical adsorption (Activation Energy). The adsorption is fast and low, and the process is frequently irreversible, with strong chemical bonds [4]. Also, it has a specific position because it is carried out on low-energy adsorption phases. Chemisorption to stable motivation energy compared to the similar surface and varied in respect to the miscellaneous layer is required for adsorbent energy [6]. Chemical adsorption is characterized by a mono phase of adsorbent adsorption on the adsorbent's layer.

## **Adsorption kinetics**

For solid-liquid layer sorption processes, many attempts have been made to create a common equation characterizing the kinetics of sorption on solid layers [8]. The ability to estimate the adsorption rate is useful when constructing a batch adsorption process. The kinetics of solute intake must be known in order to choose the best working circumstances for a full-scale batch system [9].

The solute removal rate that regulates the sorbate's residence duration in the solid-solution interface is referred to as adsorption kinetics [10]. The PFO and PSO were utilized d to study the adsorption kinetics of metal ions [11].

### **Pseudo first order model (PFO)**

The initial adsorption of a solute onto an adsorbent is described by the pseudo-first-order model, sometimes referred to as the Lagergren model:

$$
\frac{dq_t}{dt} = k_1 \left( q_e - q_t \right) \tag{1}
$$

while  $\boldsymbol{q}_t$  is the adsorbate adsorbed onto the adsorbent at time *t* (mg/g),  $q_e$  is the equilibrium adsorption capability (mg/g), and  $k_{_I}$  is the rate constant per minute. From



Figure 1. (a) Adsorption process, (b) the adsorption mechanisms displayed by the linear model [7], and (c) relations between the three constituents of an adsorption process.

*t*=0 to *t*=*t*, and  $q_t$ =0 and  $q_t$ =  $q_t$ , the integral of Eq. (1) produces a linear formulation of PFO, Eq. (2).

$$
ln(q_e - q_t) = ln(q_e) - k_1 t
$$
 (2)

Plotting ln  $q_e$ -  $q_t$  vs. *t* gives us the value of  $k_i$ . Even though certain analyses have discovered to grow with or without initial solute quantity (C0), the rate constant is usually reversely proportional to the solute's initial quantity. A higher starting solute concentration requires a longer period. Variations in experimental conditions, which alter the regulating mechanism, affect the model's validity. During Henry's administration, the level of PFO fluctuates due to adsorption and the use of a high sorbent dosage [12].

In order to apply Equation 2 to an actual situation, it is necessary to have knowledge about the equilibrium sorption capacity  $q_{_e}$ . In many circumstances,  $q_{_e}$  is unknown, and because chemisorptions are sluggish, the amount sorbed is still much less than the equilibrium amount [9].

#### **Pseudo second order (PSO) model**

It is assumed in the pseudo-second-order model that the accessible phases of the adsorbent have a direct correlation to the rate of solute adsorption. The reaction rate is directly related to the quantity of active regions present on the adsorbent's layer—the driving force  $q_{_e}\!\!\text{-}$   $q_{_t}$  is proportional to the amount of solute on the surface of the adsorbent [13, 14]. The curvilinear form of PSO is seen in Eq. (3):

$$
\frac{dq_t}{dt} = k_2 \left( q_e - q_t \right)^2 \tag{3}
$$

PSO rate constant is  $k_{2}$ . The linear form of PSO is, when the integral bounds for t (0, t) and  $q_{_t}$  (0,  $q_{_t}$ ) are applied,

$$
q_t = \frac{t}{\frac{1}{k_2 q_e^2} + \frac{t}{q_e}}
$$
 (4)

Eq. (4) has been rearranged in different forms, Eq. (5)– (8).

$$
\frac{t}{q_t} = \left[\frac{1}{k_2 q_e^2}\right] + \frac{t}{q_e} \tag{5}
$$

$$
\frac{1}{q_t} = \left[\frac{1}{k_2 q_e^2}\right] \frac{1}{t} + \frac{1}{q_e}
$$
 (6)

$$
q_t = q_e - \left[\frac{1}{k_2 q_e}\right] \frac{q_t}{t}
$$
 (7)

$$
\frac{q_t}{t} = k_2 q_e^2 - k_2 q_e q_t \tag{8}
$$

The dispersion of the error function of the identical kinetic model is determined by the method employed to linearise the curvilineal role of PSO. When compared to other linearized PSO equations, Eq. (5) produces superior fitting results. As a result, a chart of *t=q<sub>t</sub>* vs. *t* can be used to derive the PSO constants. Although pH, dosage quantity, particle size, and temperature may alter the PSO model, the model examines the effect of detectable rate factors.

The initial solute consumption and adsorption capabilities of an adsorbent may be detected using PSO. The adsorption process is not chemisorption, as previously thought, since PSO has been demonstrated to be more experimentally suitable in the past 20 years. This has led to the misconception that electron transfer occurs between the adsorbate and the adsorbent. A basic fit to the PSO model cannot explain the adsorption mechanism.

While the solute quantity is low, Eq. (5) best describes the adsorption mechanism, however, when the starting concentration is high, the PFO model is preferred [15]. This occurs due to the direct relationship between low C0 and the gradual growth in  $n_q$ <sub>e</sub>-  $q$ <sub>t</sub>, resulting in the elevation of the error function. Conversely, high C0 leads to an exponential fall in ln  $q_{_e}$ -  $q_{_{t'}}$  causing a reduction in the error function. Although linear forms have been more widely used, they might be misleading for building kinetic systems.

### **Elovich model**

To further understand the chemisorption nature of adsorption, Elovich model (developed by Zeldowitsch) is applied [16]. This model helps to predict the mass and surface diffusion, activation and deactivation energy of a system. Although the model was initially applied in gaseous systems, its applicability in wastewater processes has been redeemed meaningful. The model assumes that the rate of adsorption of solute decreases exponentially as the amount of adsorbed solute increase.

$$
\frac{dq_t}{dt} = \alpha \, e^{-\beta q_t} \tag{9}
$$

As  $q \approx 0$   $\frac{dq_t}{dt} \approx \alpha$ *dq* , which is the initial adsorption rate (mg/g.min), and *β* is desorption constant. Integrating and applying the limits for  $t$  (0, $t$ ) and  $q_t$  (0, $q_t$ ), the Elovich model can be linearized as;

$$
q_{t} = \frac{1}{\beta} \ln \left[ t + \frac{1}{\alpha \beta} \right] - \frac{1}{\beta} \ln (\alpha \beta) \tag{10}
$$

As the system approaches equilibrium *t*  $\alpha\beta$  , thus Eq. (11) becomes:

$$
q_{t} = \ln \left[ \alpha \beta \right] + \frac{1}{\beta} \ln t \tag{11}
$$

The graph of  $q_t$  vs  $t$  helps to determine the nature of adsorption on the heterogeneous surface of the adsorbent, whether chemisorption or not. A number of solutes have been reported to follow Elovich kinetics model [17-19].

#### **Adsorption isotherms**

Isotherms are mathematical equations used to describe the adsorption behaviours of a particular adsorbent-adsorbate combination [20]. The adsorption isotherm indicates how the adsorbed molecules distributed between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purpose [21]. There are many basic isotherm models, which include: Langmuir, Freundlich, Temkin, BET, D-R model and others [22]. The Langmuir and Freundlich adsorption models are widely used because they are convenient to describe experimental results in a wide range of concentrations [23].

### **Adsorption isotherms**

Isotherms are mathematical equations that precisely depict the adsorption characteristics of a specific combination of adsorbent and adsorbate [24].

While the adsorption process approaches a state of equilibrium, the adsorption isotherm illustrates the distribution of interconnected particles between the solid and liquid phases. The process of fitting isotherm data to different isotherm models is a crucial step in identifying the best suitable model for design purposes [21]. Langmuir, Freundlich, Temkin, BET, D-R model, and others are examples of basic isotherm models [22]. Because they are suited to represent practical data in a wide range of concentrations, the Langmuir and Freundlich adsorption models are commonly utilized [25].

#### **Langmuir model**

The Langmuir model for single-layer adsorption onto a phase with a limited number of similar adhesion zones is a fairly simple theoretical model [26]. Depended on the following chief expectations, the equation is appropriate for homogenous processes while the adsorption operation has identical activation energy: (a) particles are linked at a set number of clear-explained placed zones, (b) each layer can only retain one adsorbate particle, (c) all zones are powerfully equal, and (d) molecules adsorbed on neighboring sites have no interactions [27].

The general Langmuir equation looks like this:

$$
q_e = \frac{q_m K_L C_e}{1 + K_L C_e}
$$
 (12)

The equilibrium adsorption capability is  $q_{_e}$  (mg/g), while the highest quantity of ions linked per unit mass of the adsorbent is  $q_m$  (mg/g). At a high equilibrium ions quantity *Ce* (mmol/L) and experimental detecting adsorption efficiency, the latter also characterizes the creation of a complete monolayer coverage on the surface. The Langmuir equilibrium constant K<sub>L</sub> (L/mmol) is connected to the affinity of the binding sites and also reflects the adsorption reaction linking energy between adsorbate and adsorbent (Fig. 1b).

### **Freundlich isotherm**

The Freundlich expression is an empirical equation that can be used to calculate non-ideal adsorption on various phases and poly-layer adsorption [28]. The model is described as follows:

$$
q_e = K_f C_e^{1/nf}
$$
\n(13)

 $C_{e}^{1/nf}/q$  $\frac{1}{|q|}^{1/ \eta f}$  /  $q_e$  <sub>is constant at a stated temperature if the</sub> quantity of the solute in the solution at equilibrium, Ce, is increased to the power of 1/n*f* with the quantity of solute adsorbed,  $q_e$ . The dimensionless 1/nf represents the power or strength of the reaction and recommends the favorability and capability of the adsorbent/ adsorbate process, whereas  $K_{\!f}$  is a relative indicator of adsorption efficiency. n*f* > 1 shows good adsorption circumstances, according to the hypothesis.

### **Sips isotherm**

The Sips isotherm model integrates the Langmuir and Freundlich isotherm models, aiming to provide a more accurate characterization of a heterogeneous surface compared to its individual constituent models. The Sips isotherm approaches the Freundlich isotherm at low adsorbate concentrations, while it closes the L isotherm at large amounts [29]. The model can be expressed as follows:

$$
q_e = \frac{q_m (K_s C_e)^{n_s}}{1 + (K_s C_e)^{n_s}}
$$
(14)

While  $q_m$  (mg/g) denotes the greatest quantity of ions linked per unit weight of adsorbent,  $K_{\rm s}$  (L/mg) denotes the Sips constant referred to the energy of adsorption, and  $n_{\rm s}$  is the system heterogeneity parameter.

#### **The Dubinin-Radushkevich (D-R) isotherm**

The data were exposed to the Dubinin-Radushkevich (D-R) isotherm model in order to determine the variability of the adsorption phase powers and the adsorbent's distinctive porousness [30]. The D-R isotherm is written in linear form as follows:

$$
\ln(q_e) = \ln(q_D) - B_D \left(RT \ln\left(1 + \frac{1}{C_e}\right)\right)^2 \quad (15)
$$

The apparent energy of adsorption, *E* was calculated by

$$
E = \frac{1}{(2B_D)^{1/2}}
$$
 (16)

The unchangeable the theoretical saturation capacity is represented by  $q_{_D}^{}$ (mol/g), and BD (mol<sup>2</sup>/J<sup>2</sup>) represents a constant that specifically denotes the average amount of energy required for the adsorption of one mole of the adsorbate. *R* represents the ideal gas constant, which has a value of 8.314 J/mol K. *T* refers to the temperature at which adsorption occurs, measured in Kelvin. *E* represents the mean free energy of adsorption per molecule of the adsorbate as it moves from an infinite distance in solution to the solid surface.

The Sum of Squares of Errors (ERRSQ) tool was used to determine isotherm parameters across the concentration range examined [28].

$$
\sum_{i=1}^{p} \left( \mathbf{q}_{e, exp} - \mathbf{q}_{e, calc} \right)^2 \tag{17}
$$

### **Temkin isotherm**

According to the Temkin and Pyzhev in 1940, adsorption is a multi-layer process. Extremely high and low values of the adsorbate's liquid phase concentrations are disregarded [7]. It considers the impact of indirect adsorbate/adsorbate interactions on the adsorption process and makes the assumption that an increase in surface area would linearly reduce the heat of adsorption ( $\Delta H$ ads) of all molecules in the layer. Only an intermediate range of ion concentrations are suitable for the Temkin isotherm. The linear form of Temkin isotherm model is given by the following Eq. (23) [31]:

# **The Temkin constant (bt ) is related to the heat of sorption (J/mol)**

$$
q_e = a_t + 2.303 \,\bar{b}_t \log C_e \tag{18}
$$

#### **Factor Influencing on Adsorption Process**

#### **pH effect**

One of the most critical parameters impacting the adsorption and ionic exchange processes in clay minerals is the pH of the solution [32].

The pH of a solution impacts the exterior phase charge of adsorbents, as well as the degree of ionization and speciation of various impurities. Changes in pH affect the adsorptive mechanism by dissociating the functional groups on the adsorbents' surface active sites. The reaction kinetics and equilibrium characteristics of the adsorption system alter as a result [33]. This is partly due to adsorbate's severe competition with hydrogen ions [34]. The adsorption process on the adsorbent layer may be explained by examining the competitive adsorption between  $\mathsf{H}_{\mathfrak{z}}\mathsf{O}^*$  and OH<sup>-</sup>ions, which offers valuable understanding of the adsorption of various anionic and cationic species. The existence of  $H_3O^+$  ions causes the phase to adsorb anions at lower pH, whereas the deposition of hydroxyl ions causes the adsorbent surface to be active for the adsorption of cations at higher pH [33].

Metal absorption is influenced by the active sites as well as the metal ion composition in the solution. At low pH,  $H_3O^*$  predominates and occupies the adsorbent's binding sites, but at high pH,  ${\sf H_3O^*}$  concentration declines and hydroxyl ions concentration rise on the adsorbent layer. As a result, the phase charge of the adsorbent shifts to negatively charged sites, increasing cation attraction [35].

### **The influence of temperature**

The temperature has two significant impacts on the adsorption system. A decrease in liquid viscosity at higher temperatures enhances the rate of adsorbate dispersion through the outer boundary phase and in the inner holes of the adsorbate molecules. Another effect is the adsorbate's equilibrium capacity, which varies relying on whether the operation is exothermic or endothermic [36].

The heat of adsorption can explain the increase and reduction of adsorption % with temperature, if adsorption decreases with increasing temperature, it could be a sign of physical adsorption. Adsorption heat is negative, and the adsorption reaction is exothermic, hence lower temperatures are favored [37].

The decrease in adsorption as temperature rises shows a weak adsorption connection between the adsorbent's phase and the metal ion, implying that physisorption is supported. Chemisorption, on the other hand, is usually the opposite, and the reaction is endothermic [38]. The rate of dispersion of the adsorbate particles between the exterior boundary phase and the inner holes of the adsorbent molecule increases with temperature, but the reduction occurs when the solution has high viscosity due to the presence of highly concentrated suspended particles. [39]. At high temperatures, on the other hand, the thickness of the boundary layer reduces due to the increased tendency of the adsorbate to escape from the adsorbent layer into the solution phase, resulting in a decline in adsorption [40].

#### **The influence of Surface area**

The particle size of the adsorbents has a direct impact on the final solute concentration and overall effectiveness of the adsorption process. Due to the lower specific surface area of larger particles, ultimate uptake will be reduced. New active sites are created as the surface area of the adsorbent grows, allowing for additional solute molecule binding [41].

Because adsorption happens primarily on the exterior of the grains and only somewhat interior of the grains because only a few of the inner efficient sites permit the metal ion to migrate within, the rate of granularity of the maze material has a substantial impact on adsorption. As a result, as particle size decreases, the adsorption surface area increases, increasing the number of appropriate adsorption zones [4].

#### **Effect of adsorption time**

Because it gives an understanding of the adsorption process' equilibrium duration, contact time is also one of the most important characteristics in all transfer phenomena, such as adsorption [42].

Because there were a great number of empty layer zones accessible for adsorption within the early steps of adsorption, adsorption was quick. The process then slowed and stayed unchanged, suggesting that equilibrium had been reached and that more molecules had accumulated on the adsorbent site. Metal ions occupy the surface adsorption sites when they become saturated [43].

## **Influence of adsorbent dose**

Also, the adsorbent dose has an essential effect on the adsorption process, with a change in adsorbent dosage, the removal percentage or adsorption capacity increases, indicating that more exchangeable sites for metal ions are available [43]. Expanding the active site on the adsorbent facilitates the ingress of metal ions into the

removal site. The attractive interaction between ions and the adsorbent surface also increases. When ions in a solution encounter an immiscible phase (solid, liquid, or gas), they tend to accumulate at the interface between the two phases. This phenomenon exerts a substantial influence on several natural and industrial systems. Upon contact between a solid surface and most aqueous solutions, ions are rapidly and effectively eliminated [44].

### **Practical application of adsorption**

#### **Applications in the industrial sector**

The following are the most basic practical uses of adsorption and related fields:

- 1. Isolation and clarification of liquid and gas matrixes, bulk components, air, and isomers.
- 2. Dehydrating gases and liquids before putting them into an industrial process.
- 3. Impurity eliminate from gas and liquid medium.
- 4. Water clarification and Chemical restoration from industrial and exhaust gases.

Selective adsorption of certain compounds from their components is used in industrial adsorption technologies for isolating gas and liquid matrixes.

Purification of gas and liquid mixes, as well as draining of some commercial gases, follow the same principle. The pore system of adsorbents employed for these applications is adequately broad to allow quick dispersion, isolation is mostly achieved through selective adsorption, which is based on van der Waals interactions among the adsorbent and the components of the gas or liquid mixtures. In the chemical and petrochemical industries, the processes listed above are key unit operations [45].

Both steric and kinetic mechanisms are used to achieve adsorption separation and purification. Both are commonly considered equilibrium separation procedures [46].

Microporous adsorbents like zeolites, which have uniformly sized windows in their crystallographic lattice structure, have a steric separation process. Just small, properly structured particles can disperse into the adsorbent area in their case, whereas all other molecules are completely excluded. The draining of steam from cracking procedures over 3A zeolite and the sorbet

systems are the two most common uses of steric separation [47]. The isolation of n-paraffins from iso-paraffins and cyclic hydrocarbons utilizing 5A zeolite is one of the most essential processes that sorbex technology can perform [48]. Draining of natural gases, liquid paraffins, solvents, and CO<sub>2</sub> removal from natural gases are some of the areas where more examples of steric separation mechanisms are used [46].

#### **Water purification**

Water treatment is one of the most common applications of ACs for liquid-phase adhesion. Synthetic organic compounds (SOC) have been found in public water systems at alarmingly high levels in recent years. Hundreds of SOCs have been found in drinking water sources, including pesticides, herbicides, detergents, polycyclic aromatic hydrocarbons, nitrosamines, phenolic components, trihalomethanes, and other contaminants.

Natural organic material (NOM), however, is present in varying quantities in all natural water sources. It is an intricate mixture of compounds formed in the environment via the decomposition of animal and plant components. The bulk of natural organic matter (NOM) consists of small hydrophobic acids, proteins, and amino acids, as well as larger humic and fulvic acids. The interactions of NOM with purifications for example chlorine can result in decontamination by-products, such as chlorophenols and halomethanes, which are the most prevalent chlorination by-products. Many of these organic chemicals are known to cause cancer. Several strategies for controlling organic pollutant contamination of water have been tried, with varying degrees of effectiveness. Activated carbons, on the other hand, are currently the greatest broad-spectrum technique available. As a result, activated carbons are increasingly being used in water treatment around the earth. Grainy activated carbon (GAC) adsorption is a proven method for removing organics from potable water while also enhancing its flavor and odor. It also enables the elimination of trace metal ions from the water, for example, Cd, Cr, Hg, Cu, Fe, V, Zn, and Ni. ACs are currently being utilized in much higher quantities. GAC's adsorptive capability and selectivity, stability and capability to endure thermal recovery, and opposition to corrosion losses during transportation and handling are all important qualities for water treatment [49].

In the last three decades, the usage of GAC for purifying public and industrial sewages has grown dramatically. Moving beds, fixed beds with a downward flow, and expanding beds with an upward flow have all been employed in industrial wastewater applications. Carbon adsorbents are rarely used on a throwaway basis in most wastewater applications due to their high initial cost. Thermal remotivating of hard-coal-based carbons has thus been shown to be the most powerful method. Chemical recycling is typically used in situations where partial capacity recovery is allowable and regenerate disposal is not a concern [49].

#### **Environmental utilizations**

Each part of the individual movement is inextricably linked to the natural world. Every day, we interact with and affect our environment, whether we are conscious of it or not. The rapid advancement of technology, particularly at the close of the twentieth centenary, has greatly expanded human's capability to manufacture commodities, hence raising their level of living. On the other side, this improvement has resulted in a secondary phenomenon: contamination of the earth. As a result of this effect, the quality of life has deteriorated. As a result, the improvement of life quality as a result of innovative technologies has had detrimental consequences on the environment. Appropriate technologies that seem to be an important motivating power to enhance the earth should be employed to maintain an equilibrium between technology improvement and the primary constituents of the human environs [50]. It is necessary to design suitable actions for improving the feature of spring water, potable water, soil, and air. Environmental changes have an impact on human health as well as the preservation of the world's wildlife and flora. Just a few chemical chemicals found close to humans can be deemed advantageous to one's health. Even at little dosages, the majority of them are dangerous to humans. They can be found in all of our environmental medium, including air, water, and soil, which is why we must intensify all efforts related to individual environmental preservation. The capabilities and outcomes of contemporary chemical studies of contaminants in biological fluids to protect man health are some of the most crucial variables in this field [48].

The most crucial element in our earth is water. Potable water is becoming increasingly hard to find in today's world, but our need for it is increasing. The increased amounts of fertilizers like nitrates and phosphates in surface water are a major issue [51]. Many rivers, lakes, and other containers have had their water quality deteriorate as a result of their existence. As a result, adsorption methods [52], ion-exchange [53], and suitable biotechnological approaches must be used to remove nutrients originating from sewages and fertilisers. Eutrophication in closed water systems is caused by phosphorus and related components diffused in subsurface waters, particularly in lakes and strongly closed bays where water stagnates [54]. Slag medium, which are discarded side products of the steel industry, are efficient phosphorus and compound adsorbents [55].

Our environment is primarily made up of the earth's atmosphere and water. The inclination to reduce the cost of making items by using polluted starting materials without cleaning or enriching them before use is one of the major causes of air pollution. Preliminary coal desulfurization is relatively uncommon. When air is utilized as an oxygen source, nitrogen in the atmosphere acts as a diluent, that is expelled into the air with other pollutants after oxygen consumption. Another type of air pollutant is dust and haze. To avoid an increase in the amount of heat diffused into the atmosphere, modern adsorption methods should limit carbon dioxide emissions [56]. The 'greenhouse effect,' which causes a shift in climate, is the result of this growth. Another major issue is the elimination of (VOC) components from spring water, as well as the restoration of chlorofluorocarbons (CFCs), that are still utilized in glaciation and chilling processes. Controlling CFC emissions to prevent ozone depletion is critical [49].

The industry is under increasing pressure to reduce harmful emissions into the environment. A wide range of technologies for controlling and removing both natural and genetic, civil, farming, and other impurities have been developed and are available. Adsorption technologies are the most essential strategies for overcoming the continual degradation of environmental quality in terms of price-performance ratio. They have a crucial role in the management of environmental and human health, as well as in mitigating global warming and reducing ozone depletion. The imperative to limit the concentration of ozone-depleting substances, such as chlorofluorocarbons (CFCs), in the Earth's atmosphere. The rise in interest in adsorption technologies can be attributed to the usage of conventional compressor heat pumps in cooling operations and the need for primary power diversification in the air conditioning industry [49]. Adsorption operations constitute the foundation of several energy technologies designed for

safety, which may be employed in domestic and industrial environments. These technologies include reversible adsorption heat pumps, cooling processes, and heat transformers that utilize industrial waste heat as their primary energy source. They can also be employed for transportation-related applications, such as automobile air conditioning or food preservation.

Adsorption-based drier dehydration is also gaining traction as a cooling and air-conditioning alternative to vapor compression systems. Because of the high adsorption of air contaminants by desiccant materials, a drier-based process can develop interior air character and eliminate contaminants. Furthermore, the desiccant removes or kills a number of bacteria. Other issues include drinking water production, anthropogenic pollution removal from air, soil, and water, and microorganism removal from indoor air [49]. Adsorption technologies are given major tasks by them. Adsorption may also play a part in environmental management and life-supporting operations or planetary bases, where sorbents may be utilized to operate home air or collect beneficial compounds from local ecosystems. Gravity independency, excellent dependability, relatively high power capability, design flexibility, technological maturity, and recyclability make adsorption technologies good applicants for isolation and clarification in space. As a result, adsorption has long been a significant component of life support aboard the manned US and Russian spacecraft [57]. The elimination of SO<sub>x</sub> and NO<sub>x</sub> from hot ignition gases is another environmental issue. Advanced adsorption techniques may be used to tackle the challenges outlined above [49]. The quick press oscillates adsorption PSA. techniques, for example, are extremely effective in addressing both world and local earth challenges [49, 58]. The term "world environmental argument" refers to the release of ozone-reducing gases such as CFCs and VOCs, as well as "greenhouse" gases such as  $\mathrm{CO}_{2'}$ , CH<sub>4</sub>, N<sub>2</sub>O, and others. Flue gas recovery SO<sub>x</sub> and NO<sub>x</sub>, solvent steam fractionation and solvent steam recovery, sewage remedy, and drinking water production are all examples of local environmental problems. Other environmental concerns include industrial solid mists, which are insufficient ignition products. Many hurtful organic compounds can be absorbed by their surfaces. Adsorbed and chemisorbed species may be transformed into even more poisonous forms by thermal and photochemical processes. These can be administered to humans via the reparable portion of mists or potable water. As a result, solid mist surfaces are dangerous as precur-

sors to the formation of powerful toxics, carcinogens, and mutagens. Solid mists can mix with various forms of organic and inorganic contaminants in the atmosphere, resulting in unanticipated chemical combinations. The study of organic pollutant adsorption and chemical reactions on industrial-mist layers is a significant earth concern [49].

Biosorption is the process of metals adsorbing into living or dead cells. Metal-microbe interactions are addressed by biosorption in both terrestrial and marine environments. In aqueous systems, biosorption by sea bacteria is important for heavy metal detoxification. The research on the role of biosorption in the production of metal crystals is limited. In terms of the effect of cell exterior layer S-phase. constituents on crystal habit, the role of microbes in nucleation and halite crystal formation is crucial [49].

Only a small portion of the issues in which adsorption ways play a critical role has been discussed. However, as a result of the preceding factors, the topic of current adsorption technology utility has huge environmental, economical, and legal implications. It poses significant defiance in terms of the potential for continuing rapid development.

#### **Sewage remedy by adsorption**

Adsorption is a process of separating the components of a fluid, liquid, or gas by causing them to adhere to the outer and inner surfaces of a solid substance called the adsorbent. The isolation relies on the selective adsorption of contaminants by an adsorbent, namely due to thermodynamic and/or kinetic selectivity, resulting from particular interactions between the surface of the adsorbent material and the trapped pollutants. Direct transmission of weight from the liquid layer to the solid layer [59]. The adsorbent, the adsorbate, and the sewage, e.g., pollutant, artificial solution, or water, are all implicated in this surface phenomenon, which is the result of intricate interactions among the three components. The three components and their interactions are depicted schematically in Fig. 1c. The fundamental interaction force influencing adsorption in this ternary process is, in general, the affinity between the adsorbent and the adsorbate [60]. Adsorption can be affected by the affinities between the adsorbate and the solution, the adsorbent and the solution, and the pollutant particles. Hydrophobic compounds have a restricted ability

to dissolve in a water-based solution and are compelled to accumulate on the adsorbent layer. It is reasonable to infer that the contact forces between the three adsorption particles will impact the adsorption capacity.

#### **Material types for pollutant removal**

### **Adsorbents categorization**

Adsorbents composed of solid compounds are available in various chemical compositions and geometric configurations. This is evaluated based on the wide range of applications they have in industries and their usefulness in laboratory experiments. Adsorbents are

commonly categorized into five distinct types: (1) Organic materials such as sawdust, wood, fuller's earth, or bauxite, (2) Organic materials that have been utilized for improve their compositions and qualities, for example, AC, alumina, or silica gel, (3) synthetic components like polymeric resins, zeolites, or aluminosilicates, (4) agricultural solid wastes and industrial side products like date pits, fly ash, or red mud, and (5) biosorbents like chitosan, fungus, or bacterial biomass Crini and Badot [61] proposed a simplified classification system that divides adsorbents into two categories: conventional and non-conventional.





Traditional commercial adsorbents, such as ACs, ionexchange resins, and inorganic materials including activated aluminas, silica gel, zeolites, and molecular sieves (which are not exactly zeolites), can be categorized as examples (Fig. 1d). The commercial application of adsorption has been dominated by only four kinds of generic adsorbents: activated carbons, zeolites, silica gel, and activated aluminas [62]. ACs derived from agricultural solid impurity and commercial side products, natural components like clays, commercial side products for example red mud, biosorbents like chitosan, and various adsorbents like alginate are among the nonconventional adsorbents (Fig. 2).

#### **Commercial activated carbons**

Most contaminated bodies of water include significant amounts of organic and mineral pollutants that are dangerous or otherwise unsatisfactory due to their ability to generate odor, disagreeable taste, and color, among other undesirable effects [63]. Among the several methods for removing pollutants, the use of ACs for liquid-solid adsorption is the most effective and versatile approach. This method may successfully target and eliminate a wide range of contaminants [49, 64]. Undoubtedly, carbons are among the oldest and widely used adsorbents in the industry. Commercial air conditioners are very efficient adsorbents due to their exceptional potential to adsorb pollutants. When the adsorption process is properly designed, they yield output of superior quality. Their capacity to perform is mostly derived from their structural characteristics and porous texture, which provide a large surface area. Additionally, their chemical composition may be easily altered by chemical treatment to modify their capabilities. It is customary to employ AC in batch mode for treatments using these adsorbents. This can be done by either adding AC to a container with the contaminated solution or by continuously passing the solution through a carbonpacked bed. In general, industrial air conditioners are used as effective adsorbents for organic matter in secondary and/or tertiary treatment processes. They are particularly useful in filtering highly polluted emissions from the textile sector, which are characterized by color, chemical oxygen demand, and total organic carbon. Examples of adsorbents with a wide range include pesticides, aromatic and phenolic derivatives such as polycyclic aromatic hydrocarbons and polychlorobiphenyls, as well as pharmaceutics, VOCs, hydrocarbons, surfactants, minerals with metals, and molecules that cause water discoloration. Additionally, substances with a dis-

tinct flavor or odor can also be considered adsorbents. Additionally, they include hazardous organic compounds that are not easily treated upstream, or they complete the elimination of organic waste at the final stage of commercial emission treatment before being released. Moreover, macroporous activated carbons can serve as substrates for bacteria, which can degrade a fraction of the adsorbed organic substances (biological clearance). This process aids in the renewal of the sorbent in its original location. Typically, this treatment is supplemented with an ozonation phase, which enhances the efficiency of the procedure to a greater extent. Activated carbon biological filters are employed to detoxify ion-loaded effluent, eliminating substances such as iron, manganese, and nitrate. They are also utilized to decrease biochemical oxygen demand, chemical oxygen demand, and total organic carbon [65]. The use of industrial air conditioners as a remedy also has the benefit of generating no byproducts, unlike chemical oxidation. The utilization of AC powder, in conjunction with an ultrafiltration layer or other methods such as oxidation, offers a cost-efficient technological solution, especially in the realm of water recovery. AC has completely substituted oxidation with ozone and competes favorably with nano filtration.

ACs have been utilized for an extended period, but they are consistently undergoing advancements, particularly due to the increasing need for highly purified water. Currently, there is a strong focus on advancing new types of components such as AC cloth and nanotubes, as well as understanding the mechanisms behind motivation, sorption, and recycling. This includes exploring microwave technologies and heat-free processes. These areas are currently the subject of intense study in both fundamental and practical applications [66].

However, activated carbon technique does have numerous disadvantages. Industrial air conditioning systems are characterized by their high cost and lack of selectivity, meaning that the greater the quality or grade of the system, the more expensive it is. There exist several varieties of carbon, which vary not only in the type of raw material used but also in the carbonization settings and physiochemical activation methods applied. While the impressive adsorptive capacity of active carbons is well acknowledged, the challenge lies in the proper disposal of old ACs, as well as the drawback of their quick saturation and subsequent need for replacement. The process of regenerating saturated carbon is highly

expensive, time-intensive, and leads to detrimental effects on the adsorbent material. Due to these issues, the overall usage of this therapy is restricted. In particular, small and medium-sized firms are unable to afford it due to its exorbitant cost [67].

#### **Other commercial materials**

Multiple studies have been undertaken to assess the potential of alternative commercial adsorbent materials as substitutes for activated carbons [68]. Zeolites, industrial activated alumina, silica gels, ion-exchange resins, and sand are commonly employed in considerable quantities [62]. The resins mitigate the release of polluted water into the surroundings and have been successfully employed to eliminate mineral and organic contaminants, such as different types of dye particles from washing water and metallic impurities from pickling baths. Ion-exchange has various benefits, such as the absence of adsorbent degradation during regeneration, the recovery of solvents after use, and the removal of soluble contaminants at low concentrations. These materials, such as industrial air conditioners, are costly (excluding sand), which is a significant factor to take into account [67].

### **Non‐conventional green adsorbents**

Despite the fact that these industrial elements are superior to traditional adsorbents for pollutant removal, their extensive industrial application is limited because of their high cost. In addition, Streat et al. [69] argued that using industrial carbons derived from expensive raw materials is not warranted for the majority of pollution control and environmental applications. Consequently, alternative non-traditional adsorbents were introduced, examined, and utilized as cost-effective and efficient adsorbents. These principally include byproducts and derivatives from biological, commercial, and agricultural sources, as well as those derived from forest industries (referred to as green adsorbents). Among the substances included in this category are algae, bacteria, fungus, yeasts, bark, sawdust, peat, natural products such as cotton, flax, and hemp, polysaccharides like starch, cellulose, chitosan, and alginates, commercial byproducts like red mud and sludge, plants, and new nanomaterials. The abundance, accessibility, affordability, and potential strength of these uncommon materials make them attractive due to their distinctive physicochemical features and composition. Although there has been undeniable improvement, it is important to acknowledge that the use of these components

in adsorption techniques is currently mostly limited to research laboratories [70].

#### **Adsorbents**

Although there are a variety of adsorbents utilized in adsorption ways, AC is the most widely employed in sewage remedy around the globe [71]. However, because of its exorbitant price, it is only used in limited circumstances. As a result, numerous investigations have been conducted in order to identify effective and cheap adsorbents. Metal ions are removed using a variety of adsorbents, including chitosan, eutrophic and oligotrophic marsh peat, and farming materials including wheat husk and cacao husk [72].

Due of its low cost and excellent removal effectiveness, natural clay is also a suitable adsorbent. Their huge surface area and exchange capacities contribute to their sorption abilities. Clay minerals have a negative charge on their structure, which allows them to attract metal ions [73].

For the elimination of metal ions, the current investigation has concentrated on adsorbents like biomass and polymeric polymers. Natural carbohydrate polymers, primarily polysaccharides, for example, chitosan, starch, cellulose and its derivatives, cyclodextrins, have brought special attention to sewage remedy, particularly in the elimination of metal ions, due to their physical and chemical properties, cheap, accessibility, and the existence of numerous active groups on the back chain. Natural polymers, on the other hand, have significant drawbacks that limit their utilization in actual sewage remedy utilizations, such as poor surface area and problematic isolation from the liquid layer [74].

Functional groups that have been immobilized have a significant role in improving the efficiency of adsorbents [75]. It is generally known that chelating compounds like crown ethers have a high affinity for metal ions. Due to their exceptional complex selectivity for various metal ions, they have been extensively utilized in the selective transport and extraction of metal ions [76].

#### **Cellulose**

The polysaccharide known as cellulose is a straight polymer that is composed of *β*-D-glucopyranose units that are connected by *β*-1.4 glycosidic bonds. It is the most common biopolymer in nature and is the major



Figure 3. Chemical structure of (a) cellulose, (b) starch, (c) chitosan, (d) chitin, and (e) lignin.

constituent of plant fibers, which gives them hardness. Because of its affluence, easy accessibility, and cheapness, it is considered the most effective bio-based raw material [77].

Cellulose is thus a semi-crystalline polymer, which comprises the two crystalline and amorphous states. Since it is a straight biopolymer and has two forms of (OH) groups, primary (–OH) in the methylol group at C-6 and secondary (–OH) at C-3 and C-4 as shown in Fig. 3a, both hydroxyl groups are hydrophilic, and not dissolve due to strong hydrogen bond in water and specific solvents. Cellulose crystalline zones are formed due to the hydrogen bonding between cellulose groups and the





van der Waals forces between glucose units [78]. Cellulosic materials are widely known to be capable of being generated and utilized as cost-effective adsorbents. The efficacy of these materials in removing heavy metal ions can be influenced by chemical treatment. Chemically altered cellulose materials often demonstrate higher adsorption capacity compared to unaltered versions. A variety of chemicals, such as organic acids, bases, oxidizing agents, and organic compounds, were used for modification. Table 1 presents data on the removal of heavy metal ions from sewage water using cellulose as an adsorbent.

### **Starch**

Starch is one of the world's most abounding natural polymers (Fig. 3b). Because natural polymers and their derivatives are renewable, biodegradable, and able to adsorb metal ions by inexpensive adsorbents, some starch derivatives were widely used to remove heavy metal ions [98].

Naturally, biopolymer starch, obtained from plants, is an inexpensive, biodegradable, sustainable and abundantly accessible polysaccharide particle. Granules of starch are mostly composed of two distinct forms of alpha-glucan, which are polysaccharides that are composed of a polymer of glucose, amylose, and amylopectin. These starch granules account for approximately 98–99 percent of the total net weight of the starch. Amylose is a relatively straight a-glucan that has 1% a(1–6) and 99% a(1–4) connections, whereas amylopectin has a highly branched construction that has around 5% a(1–6) and 95% a(1–4) connections. Amylose is an a-glucan that shows a relatively straight structure. Furthermore, starch is shown to contain minimal amounts of both proteins and lipids [99].

Natural starch has restricted industrial applications because of the insolubility of its pastes and gels in water at ambient temperature, simple retro gradation and unstable. Starch functionality can be altered by various methods such as chemical, genetic and physical modification [100].

 Some chemical modification is essential to alter starch properties [101]. For example, succinic anhydride-modified starch effectively removes Copper, Zinc, Cadmium, and lead from wastewater [102]. Table 2 shows heavy metal ions elimination data for grafted starch as an adsorbent from sewage water.

#### **Chitosan**

Chitosan is a straight polysaccharide that is generated by removing an acetyl group from chitin. It is one of the most prevalent biopolymers that can be found in nature [118]. Fig. 3c reveals the chemical structure of chitosan. In addition, easy solubility, nontoxic for living bodies and easy decay, fast chemical derivation, and its capability to remove various numbers of heavy metals are the key features of chitosan. Hence, chitosan is considered a raw material for chelating resins.

Chitosan has several groups' amine and hydroxyl, which can bind metal ions, affording high removal percentage and discrimination [119]. Chitosan is widely recognized for being a remarkable biosorbent for eliminating heavy metal ions because it possesses an unprecedented mixture of properties (inclusive of biodegradability, bioactivity, biocompatibility, and nontoxicity) and it's far the richest and most inexpensive biopolymer in nature.

Nevertheless, it has some limitations (such as low acid stability, insufficient mechanical properties, little thermic constancy, defiance to mass transfer, and low pores and surface area), resulting in lower contaminant adsorption potential in wastewater [120]. Several study groups have used physiochemical techniques to prepare chitosan components to overcome these drawbacks. In other words, by transforming chitosan powder into gel (beads, membranes, film, etc.) or nano-particles, physical modification can enhance pores, surface area, and adhesion zones, enhance mechanical features, extend chitosan biopolymer series, decrease crystallinity and increase lumping and dispersion features. Chemical modification can improve chitosan's elasticity and chemical resistance, and reduce its acid media sensitivity. Currently, the methods of chemical modification include primarily grafting, immobilizing, and infusion, which take places primarily in reactive groups of chitosan (mostly –NH2 groups) [121].

Additionally, certain groups have infused distinctive reactive groups into chitosan to improve their adhesion efficiency. For example, zinc sulfide grafted chitosan was synthesized, and it has the capability to adsorb metal ions from aqueous solutions [122]. Table 3 presents heavy metal ions removal data for chitosan as an adsorbent from sewage water.



**Table 2.** Heavy metals removal by applying modified starch as an adsorbent.





| Chitosan          | Triethylene-tetramine  | Pb 2+370.63   | 6.0               | L           | $[142]$ |
|-------------------|--|---|-------------------|-------------|---------|
| Chitosan          | Polyvinyl alcohol  | Cd 2+737.5  | 6.0               | L, F        | [143]   |
| Chitosan          | Magnetite  | Pb <sup>2+</sup> 63.0<br>Ni 2+52.0                  | 6.0               | L           | [144]   |
| Chitosan          | Perlite  | $Cd^{2+}178.6$                                      | 6.0               | L           | $[145]$ |
| Chitosan          | Active blue two dye  | $Cu2+57$<br>$Ni2+11.2$                              | 7.0<br>8.5        | L           | [146]   |
| Chitosan          | Epichlorohydrin  | $Cu^{2+}81.04$                                      | 6.0               | L,F         | $[147]$ |
| Chitosan          | 2[ di (pyridylmethyl)<br>aminomethyl]-4,6-methyl<br>formylphenol | $Cu2+109$<br>$Cd2+38.5$<br>$Ni2+9.6$                | 6.0<br>2.0<br>3.0 | L           | [148]   |
| Chitosan          | Calcium alginate   | Ni <sup>2+</sup> 222.2                              | 5.0               | L           | $[149]$ |
| Chitosan          | Fe   | $As3+ 13.4$   | 9.0               | L-F         | [150]   |
| Chitosan          | Spherical polystyrene  | $Cu^{2+}99.8$                                       | 6.0               | $\mathsf L$ | [151]   |
| Chitosan          | Caboxymethyl-ß-cyclodextrin                                      | $Cu2+250$<br>$Cr^{6+}200$                           | 6.0               | L, T        | $[152]$ |
| Chitosan          | Magnetic Mn ferrite<br>nanoparticles                             | $Cu^{2+}65.1$                                       | 6.5               | L           | [153]   |
| Chitosan          | 2-aminopyridine-glyoxal (APG)                                    | $Cu2+124$<br>$Cd^{2+}84$<br>$Ni2+67$                | 5.0               | L           | $[154]$ |
| Chitosan          | Maleic anhydride   | Cu <sup>2+</sup> 132.5<br>Pb 2+246.3                | 5.0               | $\mathsf L$ | [155]   |
| Chitosan          | Clinoptilolite   | $Cu2+11.32$<br>$Co2+7.94$<br>Ni <sup>2+</sup> 4.209 | 5.0               | L           | [156]   |
| Xanthate chitosan | Epichlorohydrin  | $Cu2+43.47$   | 5.0               | L           | [157]   |
| Chitosan          | Sulfydryl-functionalized graphene<br>oxide                       | Cu <sup>2+</sup> 425<br>Pb 2+447<br>$Cd^{2+}177$    | 5.0               | $\mathsf F$ | [158]   |
| Magnetic chitosan | Ethylenediamine  | $Cr^{6+}$ 1.813                                     | 2.0               | L,T         | $[159]$ |
| Chitosan          | Fe   | $Cr^{6+}295$  | 4.7               | L-F         | $[160]$ |
| Chitosan          | Bentonite composite  | $Cr^{6+}89.13$                                      | 2.0               | L           | [161]   |
| Chitosan          | Epichlorohydrin  | $Cr^{6+}30$   | 3.0               | L           | $[162]$ |
| Chitosan          | Clay nanocomposite   | $Cr^{6+}357.14$                                     | 3.0               | L           | [163]   |
| Chitosan          | Amino terminated hyperbranched<br>dendritic polyamidoamine       | $Cr^{6+}185$  | $2 - 4$           | F           | [164]   |
| Chitosan          | Activated charcoal   | $Cd^{2+}52.63$                                      | 6.0               | $\mathsf L$ | [166]   |

**Table 3.** Heavy metals elimination utilizing modified chitosan as an adsorbent. Contiuned.



# **Table 3.** Heavy metals elimination utilizing modified chitosan as an adsorbent. Contiuned.

### **Chitin**

Chitin is the second most common biopolymer from a sustainable natural source in the world. It is a polysaccharide with a long polymeric chain, and as a result, it has a lot of benefits for alteration throughout derivatives construction. Chitin is a biopolymer with a large molar mass, straight subsequent groups of β-D-(Acetylamino)- 2-deoxy-glucopyranose (binds by b-1,4 units) and it chemically looks like cellulose, in which an acetamido group has substituted the -OH group at C-2 in cellulose [190]. The crab-shrimp shell is the most plentiful source of chitin [191].

The poor adsorption efficiency however limits its utilization as an adsorbent in the elimination of metal ions from sewage water [192]. Physiochemical ways have been employed to alter its outer features to improve the adhesion efficiency of chitin [193]. Table 4 shows heavy metal ions removal data for chitin as an adsorbent from sewage water.

### **Lignin**

Lignin alone with cellulose is an essential constituent of the natural lignocellulosic polymers. This is composed primarily of three separate units of phenylpropane, namely, p-coumaryl, coniferyl, and sinapyl alcohols (Fig. 3e).

Lignin is one of the basic components of natural lignocellulosic materials present in the cell walls. This is commonly accessible as a second product from the paper & pulp, bio-ethyl alcohol factory, etc. industries. Lignin is a three-dimensional nebulous biopolymer consisting of three main units by C-O and C-C connections: sinapinic acid 3-(4-hydroxy-3,5-dimethoxyphenyl) prop-2 enoic acid, ferulic acid (2-propenoic acid, 3-(4-hydroxy-3-methoxyphenyl)- ferulic acid, and *p*-coumaryl (4-(3-hydroxy-1-propenyl) phenol alcohols [210].

**Table 4.** Heavy metals elimination utilizing chitin and modified chitin as an adsorbent.

![](_page_20_Picture_399.jpeg)

# **Table 5.** Heavy metals elimination utilizing lignin and modified lignin as an adsorbent.

![](_page_21_Picture_523.jpeg)

| Lignin           | Carboxymethylation   | Pb <sup>2+</sup> 107.5<br>$Cd^{2+}67.7$  | 6.0<br>5,0 | L           | [236]   |
|------------------|--|--|------------|-------------|---------|
| Lignin           | Dimethyl-acetoxy-(2-<br>carboxymethyl ether                        | $Cu2+399$  | 5.5        | $\mathsf F$ | [217]   |
| Lignin           | Polyoxometalate POM/H <sub>2</sub> O <sub>2</sub>                  | $Cd^{2+}35.9$<br>$Pb^{2+}155.4$  | 5.0        | ----        | [237]   |
| Lignosulfonate   | Bentonite  | Pb <sup>2+</sup> 314.8   | 5.0        | L           | [238]   |
| Alkaline lignin  | Methanamine and Methyl<br>aldehyde                                 | $Pb^{2+}60.5$  | 6.0        | $L, D-R$    | $[239]$ |
| Lignin           | $SO_{\rm a}$   | Pb <sup>2+</sup> 952   | 7.0        | L           | $[240]$ |
| Alkaline lignin  | Sulfomethylation   | Pb <sup>2+</sup> 53.8<br>$Cu2+45.4$  | 6.0        | $D-R$       | $[241]$ |
| Lignin           | 1,2,4-triazole-3-thiol   | $Cd2+72.4$   | 6.0        | L           | $[242]$ |
| Lignin           | Dithiocarbamate  | $Cu2+175.9$<br>Pb <sup>2+</sup> 103.4  | 6.0        | L           | $[243]$ |
| Lignin           | Epichlorohydrin  | Pb2+72.48<br>Cu2+55.35   | 6.0        | L           | [212]   |
| Lignin           | Poly(ethyleneimine)  | $Pb^{2+}33.9$  | 6.0        | $\mathsf F$ | $[244]$ |
| Alkaline lignin  | Xanthate   | $Pb^{2+}64.9$  | 5.0        | Г           | [245]   |
| Alkylated lignin | Carbamodithioate   | $Pb^{2+}188$   | 5.0        | L           | [246]   |
| Kraft lignin     | Silica   | Ni <sup>2+</sup> 77.11<br>$Cd^{2+}84.66$   | 7.0        | L,F         | $[247]$ |
| Lignin           | $TiO2-SiO2$<br>TiO <sub>2</sub>                                    | Pb <sup>2+</sup> 59.9<br>Pb <sup>2+</sup> 35.7                                   | 5.0        | $\mathsf L$ | $[248]$ |
| Lignin           | $MgO-SiO2$   | $Cu^{2+}83.9$  | 5.0        | Г           | $[249]$ |
| Lignin           | Carbon nanotube  | Pb <sup>2+</sup> 235   | 5.8        | L           | $[250]$ |
| Lignin           | Poly(ethyleneimine)  | $Cu2+98$<br>$Zn^{2+}78$<br>$Ni2+67$  | 6.0        | L           | $[251]$ |
| Lignin           | Alginate/hydroxyapatite  | Cu <sup>2+</sup> 79.67<br>$Ni2+71.18$  | 5.0<br>7.0 | $\mathsf L$ | $[252]$ |
| Lignin           | 5-sulfosalicylic acid  | $Pb^{2+}39.3$  | 5.35       | Г           | $[253]$ |
| Lignin           | Acrylamide, Maleic anhydride                                       | Pb <sup>2+</sup> 216.52  | $5.0\,$    | L           | [239]   |
| Lignin           | Carboxymethyl  | Pb <sup>2+</sup> 333.26  | 6.0        | $\mathsf L$ | [254]   |
| Lignin           | glycine and<br>cystine   | $Cu2+76.1$<br>$Cu2+ 81.3$  | 6.0        | L,F         | $[255]$ |
| Lignin           | Chitin   | $Cu2+75.7$<br>$Zn^{2+}82.41$<br>Ni <sup>2+</sup> 70.41<br>Pb <sup>2+</sup> 91.74 | 5.0        | $\mathsf L$ | $[256]$ |
| Lignin           | SiO <sub>2</sub>   | Ni <sup>2+</sup> 77.11<br>$Cd^{2+}84.66$   | $6.0\,$    | $\mathsf L$ | [248]   |
| Magnetic lignin  | diethylenetriamine   | $Cr^{6+}$ 123  | 2.0        | $\mathsf L$ | $[219]$ |
| Lignin           | $poly(3, 4 -$<br>ethylenedioxythiophene)/<br>polystyrene sulfonate | Pb <sup>2+</sup> 452.8   | $- - - -$  |             | $[257]$ |

**Table 5.** Heavy metals elimination utilizing lignin and modified lignin as an adsorbent. Continued.

| Lignin | sulfuration  | Pb <sup>2+</sup> 130.2  | 5.0    | Г         | [258]   |
|--------|--|---|--------|-----------|---------|
| Lignin | montmorillonite  | $Cu2+74.35$   | 6.5    | F         | $[259]$ |
| Lignin | Acetylcysteine   | $Cu^{2+}68.7$<br>$Pb^{2+}55.5$  | 6.0    | L         | [260]   |
| Lignin | polyacrylic acid   | $Cu^{2+}68.7$<br>$Pb^{2+}55.5$<br>$Cd^{2+}84.66$  | 5.0    | F         | $[261]$ |
| Lignin | poly(N-methylaniline)-graphene<br>oxide  | Pb <sup>2</sup> +753.5  | ------ | $- - - -$ | $[262]$ |
| Lignin | polyethylenimine   | $Pb^{2+}96.6$   | 6.0    | Г         | $[263]$ |
| Lignin | TiO <sub>2</sub><br>Silicon dioxide-TiO <sub>2</sub><br>Magnesium oxide-TiO <sub>2</sub><br>Titanium dioxide<br>Silicon dioxide-TiO <sub>2</sub><br>Magnesium oxide-TiO <sub>2</sub> | $Cu2+22.69$<br>$Cu^{2+}19.24$<br>$Cu2+35.99$<br>$Cd^{2+}25.12$<br>$Cd^{2+}16.7$<br>$Cd^{2+}69.97$ | 5.0    | Г         | $[264]$ |
| Lignin | Phenol   | $Ni2+12.48$<br>$Ni2+16.94$  | 7.0    | F         | [265]   |
| Lignin | SiO <sub>2</sub>   | Pb <sup>2+</sup> 89.02  | 5.0    | L         | [266]   |
| Lignin | Polyethyleneimine and carbon<br>disulfide  | Pb <sup>2+</sup> 79.9   | 6.0    | L         | [267]   |
| Lignin | -----  | $Cr^{3+}17.97$  | 5.0    | L         | $[216]$ |
| Lignin | Acrylonitrile  | $Cd^{2+}85.65$  | 4.0    | L         | [268]   |
| Lignin | Chitosan   | $Cr^{6+}111.11$   | 2.0    | L         | $[269]$ |
| Lignin | CS <sub>2</sub>  | $Cu^{2+}64.17$<br>$Pb^{2+}$ 66.7  | 4.0    | L         | $[270]$ |

**Table 5.** Heavy metals elimination utilizing lignin and modified lignin as an adsorbent. Continued.

Materials located on lignin provide a range of benefits such as biocompatibility/ biodegradability, environmentally sustainable, harmless, plentiful, inexpensive, and possessing antioxidant, ant germinal, and stabilizer features [211].

However, lignin has some limitations such as low surface area and inadequate mechanical features, which affect its use in the experimental utilization in certain work [212].

Although lignin has been applied as an adsorbent for

the elimination of many contaminants, lignin modification enhances its affinity to distinctive contaminates in the water. Therefore, it is critical to know the causes which affect lignin removal capacity, which will be of great help in the modification of lignin physical and chemical constructions and increasing the removal efficiency of metal ions in water.

Those involve the particular surface area, pore size diffusion, pore size, and surface reactive lignin groups [213]. Table 5 presents heavy metal ions removal data for lignin as an adsorbent from sewage water.

### **Conclusion**

The materials categorized in each section were tested and their adsorption ability was evaluated in this study. Polysaccharide homopolymers can be employed as biosorbents that are safe for the environment. There is an abundance of agricultural waste, such as rice husks and jute, which are sources of cellulose. The addition of additional functional groups to a polysaccharide by grafting, blending, or mixing improves its sorption capabilities as well as its mechanical qualities, allowing it to endure numerous cycles of sorption and desorption. Furthermore, functional polymers are cross-linked with telechelic polymers or monomers to boost mechanical strength. Chitosan, starch, and alginate are polysaccharides that are similar in structure and can be changed to improve sorption effectiveness.

Depending on the published publications, we present adsorption as a more effective strategy in this review. According to this study, the majority of studies indicate that adhesion or removal with the use of affordable polymer adsorbents is recognized as a more potent and cost-effective strategy for contaminating water treatment than pricey activated carbon. Through this review, we observed that cellulose and chitosan are the most used adsorbents in metal ions removal in modified and unmodified forms in comparison to the other polymers. Isotherm, optimum pH, and maximum absorption capacity.

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