Various Absorbents and Parameters Affecting Removal of Water Hardness from Wastewater: Review

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Abstract

Discharges of heavy metals from different sources to the water lead to water hardness which is the major problem of the world due to their toxic and carcinogenic nature. Among several methods to eliminate heavy metals, absorption is the leading technique for the removal of heavy metals from wastewater because it is efficient, available, low-cost, and eco-friend. This review paper gives detail information about adsorbents on both conventional and nanostructured materials, either occur naturally or available commercially. The review also contains properties and parameters which affect the adsorption process with essential clarifications that are given by researchers.

Keywords: Water hardness; Absorbents; Industrial effluent; Heavy metals

Introduction

Water is the most abundant natural resource which is essential to survive, in other words, water is life because it is used for various purposes including drinking, washing, bathing, irrigation, fire-fights, production of industrial materials, and air-conditioning [1]. However, nowadays, due to improper management of industrialization, urbanization, organic and inorganic water pollutants, and agricultural waste on the earth's surface, there is severe water pollution which is resulted in diseases like cholera, Dracunculiasis, Typhoid fever, Diarrhea, Ulcers, Hepatitis, and Arsenicosis are widely spreading across the global [2]. Among the water pollutants, heavy metals are non-biodegradable, which are easily accumulated in living things and highly toxic pollutants so that they are detrimental for human-being as well as aquatic ecosystems [3]. Some of the common heavy metal discharges from industries are Cd, Ni, Cu, Fe, Zn, Ti, Hg, Mn, Cr, As, and Pb [4,5]. When those heavy metals dissolve in water they cause water hardness. Water hardness has less health effect however leads to various disadvantages in both domestic and industrial uses. For example, domestically, water hardness causes wastage of soap during washing and more fuel consumption during cooking as well as industrially, hard water fed to the boiler leads to scale and sludge formation but mainly causes boiler corrosion at the industrial level [6].

There are some methods to eliminate heavy metals such as chemical precipitation [7], ion exchange [8], chemical oxidation [9], reverse osmosis [10], ultrafiltration [11], electrodialysis [12], and adsorption [13,14]. From those methods, the adsorption process is the most effective method for removing water hardness due to its low cost, flexibility in design, easy operation mechanism, high efficiency, availability, high-quality treated effluent, and its recyclability. While the other methods have inherent limitations like a large amount of Sludge generation, low efficiency, sensitive operating conditions, and costly disposal [13,15].

Adsorption process

The term Adsorption was first invented in 1881 by a physicist named Heinrich Kayser. Adsorption is a process in which something takes in another substance which means impurities take by the absorbent material. The molecular species that gets adsorbed on the surface is known as adsorbate while the surface on which adsorption occurs is known as adsorbent. It often goes with desorption which is the inverse process of adsorption. Desorption represents the transfer of adsorbate ions from the adsorbent surface to the solution. Nowadays, adsorption is considered an efficient as well as low-cost technique for removing heavy metal ions from wastewater [16]. This process is flexible in design and operation and allows for producing high-quality treated effluents. Furthermore, since the adsorption is reversible in some cases, adsorbents can be regenerated through desorption [13].

There are two types of adsorption called physical and chemical adsorption. Physical adsorption is in which the increase in the adsorbate concentration at the interface is due to non-specific van der Waals forces and it is weakly specific, reversible and its thermal effect is small while chemical adsorption is caused by chemical reactions between the adsorbate and the adsorbent which create covalent or

ionic bonds. In addition to these, it is selective, usually irreversible and heat ranges from tens to hundreds of kJ/mol [17-20]. The summary of the properties of physical and chemical absorbents are listed in table 1.

Adsorption phenomenon is investigated *via* experiment as well as theoretical using modeling software such as the modeling of the adsorption equilibrium data, the molecular dynamics study, the density functional theory and the characterization of adsorbent before and after adsorption. Modeling of adsorption data by isotherm is the most appropriate and widely used method. In addition to this, modeling of adsorption data by isotherm can give information of the maximum adsorption capacity, which is important to evaluate the performance of the adsorbents [21].

Modeling of adsorption data by isotherm has been applied in adsorption systems such as the Langmuir model, the Freundlich model, linear model, the Temkin model, the Sips model, and the Brunauer, Emmet, and Teller (BET) model. From these models, the linear, Freundlich, Sips, Temkin, and some other models are empirical models, those lack actual theoretical support [21]. Literally, isotherm means the relationship between the equilibrium adsorbate in the liquid-phase and the equilibrium adsorption amount on the solid-phase at a certain temperature [21].

Isotherms can be classified based on their physical meaning and theoretical derivation as empirical models, Polanyi's potential theory, chemical adsorption models which describe the monolayer adsorption process; physical adsorption models describes the multi-layer adsorption; and ion exchange models, according to their physical meanings [21].

Adsorption empirical isotherms:

• **Linear model (Henry's law):-** This model is used to represent a partition of adsorbates between solid and liquid phases. The mechanisms are Van der Waals interactions, the electrostatic interactions and hydrophobic interactions. It has the following form

$q_{e=KCe}$

Where q_e is adsorbed amount, C_e is adsorbate concentrations, and K is a partition coefficient [21].

• **Freundlich isotherm**: - This model is one of the most widely used isotherm in adsorption and used to represent nonlinear adsorption phenomenon.

The Freundlich model is given by the following equations:

$$q_e = K_F Ce^{1/n}$$

$$\log q_e = \log K_F + 1/n \log Ce$$

Where K_F and n are constants, the Freundlich model will reduce to the linear model

when n = 1 [21].

• **Redlich-Peterson (R-P) isotherm:-** This model is an empirical hybrid model of the Langmuir and Freundlich model which has been frequently used in the homogeneous or heterogeneous adsorption processes [21].

• **Sips isotherm mode:-** This model is the most applicable 3-parameter isotherm model for monolayer adsorption. It is the combination of Langmuir and Freundlich [21].

• **Temkin isotherm:-** Model in which adsorption is presumes as a multi-layer process [21].

Adsorption models based on Polanyi's potential theory: This theory assumes that the adsorption system contains an "adsorption space", where the molecules lose potential energies. The potential energies are independent of temperature, as the potential energy is reached high in the pores or cracks inside the adsorbent. Dubinin-Radushkevich (D-R) model and Dubinin-Astakhov (D-A) model are categorized under Adsorption models based on Polanyi's potential theory [21].

a) **Chemical adsorption models:** These adsorption isotherm models consider the monolayer adsorption process in which the adsorbate molecules are adsorbed in the adsorption sites of the adsorbents. Langmuir and the Volmer isotherm models are the common examples of Chemical adsorption models [21].

b) **Physical adsorption models:** This adsorption isotherm models simulate the multi-layer adsorption process. The main driving force of the physical adsorption is Van Der Waals force. Brunauer, Emmet, and Teller (BET) and the Jovanovich isotherm models are categorized under the physical absorption model [21].

Above mention theoretical discussion of the adsorption process leads scientific communities to search for material that enables to remove targeted pollutant from the medium. Since our review is target heavy metal removal from wastewater, we are going to discuss the materials have been used adsorbent in the next sections.

Materials Used for Adsorption

There are various adsorbents which are available either naturally or commercially that are used to remove heavy metals from wastewater [16]. In addition to this, adsorbents are classified as conventional and nanostructured adsorbents based upon their size and efficiency in the removal of impurity from wastewater [22]. In this part of the review, we will see the most frequently used adsorbents which are used to remove heavy metals efficiently.

Conventional absorbents

Conventional absorbents are the usual types of adsorbents for wastewater treatment [23]. They are inexpensive and available either naturally or easily synthesized from waste materials [23]. Some of the conventional adsorbents are activated carbon, Biomaterial, clay mineral and others will be discussed in the next subtitle.

Activated carbon: Activated carbon is non-graphite, amorphous, microcrystalline, tasteless, and black solid substance which is a form

Table 1: The Characteristics of Physical adsorption and Chemical Adsorption [19,20].

S/N	Properties of the physical adsorption	Properties of the Chemical Adsorption
1	It is a weak process	It is a strong process
2	The activation energy is low	This type of adsorption is almost a single-layered phenomenon
3	The force that causes the adsorption is physical forces	The type of adsorption is caused by chemical forces
4	The adsorption is not specific which means it takes place all over the adsorbent	Chemisorption is highly specific and takes place at reaction centers on the adsorbent
5	Surface area, temperature, pressure, nature of adsorbate effects the process	Surface area, temperature, nature of adsorbate effects chemisorption

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of carbon [14]. The porosity that is enclosed by a carbon atom is called activated carbon; the porosity is slit-shaped and has the size of molecules. Activated carbon is made from different materials like coal, coconut shell, hardwood, fruit stones, and synthetic molecular systems [15]. Activated carbon is an excellent adsorbent due to its high specific surface area, porosity, and various oxygen-containing functional groups on the surface [24]. As a result of such novel characteristics, it can attract and retain certain compounds in a preferential way [25]. For example, Activated carbon is used in many industrial applications including separation and purification technologies, catalytic processes, biomedical engineering, and energy storage. This is because of its wide availability, high performance in adsorption processes, surface reactivity, and the versatility to modify its physical and chemical properties for synthesizing adsorbents with very specific characteristics [26].

There are different activation agents which can be classed as physical and chemical activation agents. Some of the physical activations are steam atmosphere, air, CO_2, and Chemical activations like KOH, H_3PO_4, and $ZnCl_2$. As researches show chemical activation has been proved to be more effective with well-developed porosity than the physical activation method to prepare activated carbon [16].

Activated carbon which is coal-based is expensive so its use has been restricted so further efforts have been taken to convert the agricultural waste into activated carbon because of their availability and inexpensive nature [27-35]. In the last decades, worldwide researchers had proposed several agricultural and industrial wastes as low-cost sources to obtain raw materials for the production of activated carbon. These researchers have in mind not only to lessen its cost of production but also to diminish the environmental impact of agricultural and industrial wastes and to avoid the cost of the associated cost of solid waste handling [25].

Biomaterials: Bio adsorbents are the most advantageous adsorbent for heavy metals due to their high efficiency, availability, and there low cost [36]. Many biological materials have the potential to decrease heavy metals concentration. Some types of bio sorbents are used to remove heavy metals without specific property but others are specific for a certain metal this is the reason why biosorption takes major attention and becomes an active work area [36]. Bio-sorbents obtained from three different sources:

Non-living biomass: Non-living biomass is biomass which shows non-living things which can be obtained from different sources [37]. Non-living biomass has a great advantage over living microorganisms for removal of heavy metals due to their long time usage without any necessity of nutrient supply [37]. Some commonly used non-living biomass will be discussed as well as some of the common non-living biomasses are indicated in Figure 1.

One of the non-living biomass is sugarcane bagasse that is obtained from fibrous material after cane crushing and juice extraction it contains 50% cellulose, 27% polyposis, and 23% lignin. Sugar cane is that captivated mainly in the tropical and subtropic regions. Brazil is the world's most country to produce sugarcane followed by North America and Asia [38].

Sugarcane bagasse can be used in natural and also in modified form. Due to these biological component polymers, sugarcane bagasse is rich in hydroxyl and phenolic groups and these groups can be chemically modified to improve adsorption capacity [39]. Table 2 and 3 lists some researches done on the adsorption capacity of sugarcane bagasse for different types of heavy metals [40-45].

The other non-living biomass is wheat bran. This is a bio sorbent that gains from agricultural waste and it is one of the most economical biodegradable adsorbents which consists of important nutrients like fibers, protein, fatty acid, and minerals. Wheat bran has various organic functional groups with a large internal surface area so it can remove heavy metals from hard water efficiently [46]. The various functional groups like phenolic hydroxyl, methoxy, and carbonyl group give the material a good ability to bind heavy metals [47]. The Table 4 below shows the removal of different types of heavy metals and the adsorption capacity of wheat bran [48-51].

Nowadays many tons of coconuts are produced per year around the world especially in countries like Indonesia, the Philippines, and India. This makes both Coconut coir pith and coconut shells most available and also suitable coconut wastes for the removal of heavy metal [52]. In more than 90 countries coconut palm grown and territories of the world, over 59million tons were produced in 2016. The major counties in the world for the production over 72% of world total coconut are tropical Asia, Indonesia, Philippines, and India [53]. Coconut functional groups like hydroxyl and carboxyl lead to having the material good sorption property [54]. Table 5 shows the adsorption potential of coconut wastes used for the removal of different types of heavy metals. As indicated in this table, Coconut husk, coconut coir pith, coconut shell, and other forms of this biomass have been utilized to remove different types of heavy metals from different sources of industries [55-60].

As we all know chicken eggs are the most worldwide daily food. China is the world's top egg producer and currently, around 45% of the world's total production of an egg is held by China. The United States and India take second and third place in the production of egg respectively according to data collected in 2012 [61]. Eggshell is also one of the most waste materials across the globe which causes environmental problems as indicated in Figure 2. For example, about 150,000 tons of eggshell is disposed of in the United States every year [62]. But this material has an outstanding mechanical performance, such as high strength, an excellent combination of stiffness, impact resistance, and toughness [63]. Eggshells are used as an adsorbent for heavy metals in modified and also non modified form [64]. Here are some indicative examples of the adsorption capacity of eggshells for heavy metal removal as shown in table 6 [65-69].

The other bio sorbent is Sawdust which is produced in large quantities as solid waste at sawmills. We can obtain sawdust from
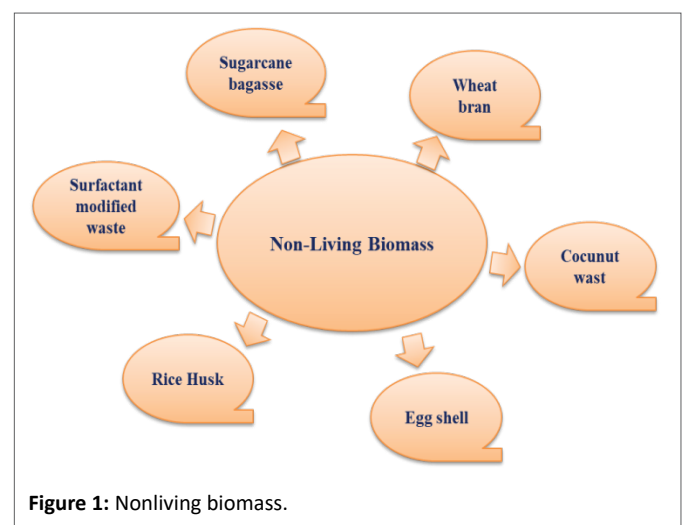

Figure 1: Nonliving biomass.

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wood by cutting, grinding, drilling, or pulverizing [70]. Sawdust contains lignin and cellulose which make it a good adsorbent for heavy metal removal [71]. The adsorption capacity of sawdust for different types of heavy metals is listed in table 7 below [72-77].

Rice husk is an agricultural waste obtained from rice mills as shown in figure 3 contains 32.24% cellulose, 21.44% lignin, 21.34% hemicellulose, and 15.05% mineral ash [78]. Rice husk is an agricultural

waste that can be obtained in many countries that produce rice. Rice husk has a granular structure, chemical stability, good mechanical strength and it is not soluble in water [79]. Silica is derived from rice husk and it results from a good affinity for chromium adsorption while modified silica by iron oxide shows the highest adsorption around 63.69 mg/g [80]. In addition to this, rice husk is one of the most silica sources we use them as adsorbents for heavy metals and many works

Table 2: Heavy metal removal using activated carbon.

S/N	Raw materials	Activation agent	Type of metal removed	Q (mg/g)	Reference
1	Jatropha wood		Chromium	106.4	[28]
2	Prawn shell		Chromium	100	[29]
3	coconut shell		Cadmium	93.4	[30]
4	Pterocladiacapillacea		Chromium	66	[31]
5	sugar beet pulp	phosphoric acid	Cadmium	68.03	[32]
6	sugarcane bagasse	Acid modified	Chromium	15.42	[33]
7	olive stones		Cadmium	17.665	[34]
8	Coconut shell fibers		Chromium	12.2	[35]

Table 3: Heavy metal removal using sugarcane bagasse.

S/N	Raw materials	Modified agent	Type of metal removed	Q (mg/g)	Reference
1	Sugarcane bagasse		Lead	47.89	[40]
2	Raw sugarcane bagasse		Mercury	35.71	[41]
3	Sugarcane bagasse	acrylonitrile and hydroxylamine	Cooper	101.01	[42]
4	Sugarcane bagasse		Cadmium	6.79	[43]
5	Sugarcane bagasse	colonized by Pleurotusostreatus	Lead	47.89	[40]
6	sugarcane bagasse	Acrylic-modified	Cooper	265.252	[44]
7	sugarcane bagasse	Sodium bicarbonate	Cooper	114	[45]

Table 4: Heavy metal removal using modified wheat bran.

S/N	Raw materials	Modified agent	Type of metal removed	Q (mg/g)	Reference
1	Wheat bran		Chromium	93	[48]
2	Wheat bran		Lead	62	[48]
3	Wheat bran		Mercury	70	[48]
4	Wheat bran	sulphuric acid	Chromium	133	[49]
5	Wheat bran	tartaric acid	Chromium	5.28	[50]
6	Wheat bran	Sulfuric acid	Copper	51.5	[49]
7	Wheat bran	Sulfuric acid	Cadmium	101	[50]

Table 5: Heavy metal removal using coconut waste.

S/N	Raw materials	Modified agent	Type of metal removed	Q (mg/g)	Reference
1	Coconut husk		Chromium	18.25	[55]
2	coconut coir pith	Amine-modified	Chromium	12.43	[56]
3	Coconut shell charcoal	oxidized with nitric acid	Chromium	10.88	[57]
4	Coir pith		Cadmium	93.4	[58]
5	Coir pith	Hexadecyl trimethyl ammonium bromide	Chromium	76.3, 1.24	[52]
6	Coconut shell carbon		Lead	26.5	[59]
7	Coir pith		Cobalt Chromium Nickel	12.82 11.56 15.95	[60]

Figure 2: Deposit of Egg shells.

Figure 3: Rice husk for removal of heavy metal.

Table 6: Heavy metal removal using Eggshell.

S/N	Raw materials	Modified agent	Type of metal removed	Q (mg/g)	Reference
1	Eggshell		Chromium	1.45	[65]
2	Eggshell		Chromium	160	[66]
3	Eggshell		Copper	44.843	[67]
4	Eggshell	α-FeOOH (F-ES)	Chromium	41.57	[68]
5	Eggshell	PEI	Chromium	160	[69]

Table 7: Heavy metal removal using sawdust.

S/N	Raw materials	Modified agent	Type of metal removed	Q (mg/g)	Reference
1	Sawdust	Sodium hydroxide	Cadmium	73.62	[72]
2	Sawdust	Sodium hydroxide	Nickel	10.47	[73]
3	Sawdust	Formaldehyde	Chromium	3.6	[74]
4	Sawdust	Sulfuric acid	Copper	13.95	[75]
5	Sawdust	Hydrochloric acid	Chromium	1.74	[70]
6	Sawdust	Formaldehyde in Sulfuric acid	Lead	9.78	[76]
7	Sawdust	Reactive Orange 13	Zinc	17.09	[77]

have been conducted and some of them are listed in the table 8 [81-83].

Lastly, surfactants also considered as non-living biomass are compounds that decrease the surface and interfacial tension and stabilize the interface [84]. The nature of their hydrophilic group leads them to be cationic, anionic, non-ionic, and zwitterion. This behavior of Surfactant modified adsorbents leads to superior removal efficiency and promote selective adsorption [84]. Agricultural wastes have been modified using various surfactants [85,86]. We can see surfactants and their effects on the removal of heavy metals on the above tables which are constructed for different kinds of non-living biomass.

Algal biomass: Alga is a photosynthetic eukaryotic large and diverse group of an organism and their biomass is used for a wide variety of applications [87]. Alga stands for singular noun and requires a singular verb while algae are for plural noun uses a plural verb. Algae have been used as fertilizer, food, and feed for centuries however currently they are used in so many applications like biomaterials, nutraceuticals, biofuels, pharmaceuticals, and bioremediation [88]. Algae used as a new adsorbent for heavy metal ion due to its availability, low cost, regular quality, and high adsorption capacity [89]. Algae are renewable natural biomass proliferating the ability to be everywhere and abundantly in the Mediterranean zones of the world. They take the attention of many researchers as organisms to be used as new adsorbents to remove heavy metals [16,89].

There are different kinds of marine algae called red algae, green algae, and brown algae the main difference between those algae is their cell walls where biosorption occurs [90]. Red algae consist of cellulose in the cell wall however the capacity of biosorption is mainly dependent on the presence of sulfated polysaccharides. Green algae also have cellulose in the cell wall but with a high content of bonded proteins. brown algae cell walls contain cellulose, alginic acid, and polymers of mannuronic and guluronic acids complexed with metals and other polysaccharides [90] (Figure 4).

Algae are also classified by size as macroalgae or microalgae [91,92].

Macroalgae: - Are multicellular, large size seaweed, and visible with the naked eye without the aid of a microscope [92]. Microalgae is a term used for seaweeds and other benthic (attached to the bottom) marine algae collectively that are visible to the naked eye. The Larger macroalgae are also referred to as seaweeds which are not really "weeds" [91]. Macroalgae have different forms, they include the simplest form with simple branching structures like simple crusts, foliose (leafy), and filamentous (threadlike), and also more complex forms include which have highly specialized structures [91]. The size of coral reef macro algae could be in the range between few millimeters to plants up to 3-4 m high [91].

Macroalgae can be classified into different "functional form" groups, based on ecological characteristics and growth form
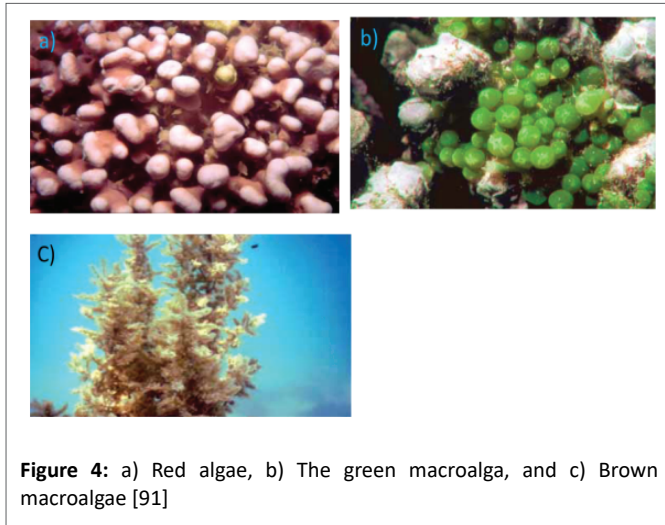
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Figure 4: a) Red algae, b) The green macroalga, and c) Brown macroalgae [91]

Table 8: Heavy metal removal using rice husk.

S/N	Raw materials	Modified agent	Type of metal removed	Q (mg/g)	Reference
1	Rice husk	Water washed	Cadmium	8.58	[81]
2	Rice husk	Sodium hydroxide	Cadmium	20.24	[81]
3	Rice husk	Sodium bicarbonate	Cadmium	16.18	[81]
4	Rice husk	Epichlorohydrin	Cadmium	11.12	[81]
5	Rice husk	Ozone-treated	Chromium	13.1	[82]
6	Rice husk	Iron oxide	Chromium	63.69	[80]
7	Rice husk	Tartaric acid	Copper Lead	31.85 120.48	[83]

instead of systematic and taxonomic classification. The Functional groups help us to understand the distribution of algal communities and their responses to environmental factors can be understood from their functional group. Algaes that have the same ecological characteristics have similar responses to environmental pressures, however taxonomically related algae mostly have different ecological properties and responses. In addition to this classification of algae in the functional approach is useful due to algae are very difficult to identify to species level, and it helps to characterize algal communities in ecological studies on coral reefs [91].

Algal turfs: Includes many species of minute algae, the major is filamentous. They have fast growth, high productivity, and high colonization rates [91].

Fleshy macroalgae: Are forms of large algal that are, more rigid and anatomically more complex than algal turfs. They are abundant in low herbivory zones [91].

Crustose algae: Are hard plants which generally have slow growth rate and they grow as crusts, adhering closely to the substrate with a painted like layer than the atypical plant [91].

Macroalgae play several roles in different area including major contributions to primary production (the basis of food-webs

forms and the overall amount of this organic matter produced in the ecosystem), bioerosion, construction and cementation of reef framework, facilitation of coral settlement, and creation of habitats for other reef species [91].

Microalgae: are single cellular, small size microscopic organisms they found in all the aquatic systems like freshwater, seawater, hypersaline lakes, and also in desserts, and arctic ecosystems [92]. Microalgae's are Subdivided into eukaryotic and prokaryotic algae, eukaryotic possessing. Outlined cell organelles such as nuclei, mitochondria, chloroplasts, and prokaryotes are primitive, possessing the simpler cellular structure of bacteria. They convert light energy and carbon dioxide (CO_2) into biomass and their mechanism in the process of photosynthesis is similar to land-based plants, however, a simple cellular structure has efficient to access water, CO_2, and other nutrients, so they are more efficient in converting solar energy into biomass [93]. The three classes of microalgae-based on abundance are diatoms (Bacillariophyceae) green microalgae (Chlorophyceae) and the golden algae (Chrysophyceae) [94].

Microalgae are energy-rich feed stocks and received so much attention due to high yields and multiple applications and also their facile adaptability to grow in the photo bioreactors or open ponds. Microalgae have many advantages such as higher productivity in a few days, they easily adapt to a new environment, and high-lipid content [93]. Microalgae can be used for several applications such as biofuels, pharmaceuticals, health supplements, and cosmetics. They are also used in wastewater treatment and atmospheric CO_2 mitigation. In addition to this microalgae are used to produce several bioproducts, like proteins, polysaccharides, pigments, lipids, vitamins, antioxidants, and bioactive compounds [92]. Microalgae are used to accumulate heavy metals from wastewater and some can degrade polyaromatic hydrocarbons and other organics. Microalgae have a very important role in wastewater treatment; they have used to the removal of heavy metals, nutrients, organic contaminants, and pathogens from waste water [94-100] (Table 9).

There are some works listed in the next table to show the adsorption capacity of algae on heavy metal removal.

Microbial biomass (bacteria, fungi, and yeast): Fungi biomass produces a high yield, is easy to grow, and also can be manipulated genetically and morphologically. Fungi bio sorbents include *Rhizopus arrhizus* [101], *Aspergillus niger* [102], *Lentinus edodes* [103], *Saccharomyces cerevisiae* etc. Despite the characteristic of broad sources, low-cost and rapid adsorption the separation of bio sorbents is difficult after the adsorption process [104].

Bacteria are the most abundant microorganisms and bacterial removal of metal ions from wastewater has been considered as being highly efficient [105]. Bacteria and cyanobacteria cell wall has the potential to capture heavy metals due to the fabric which is negatively charged group [106]. There are several processes to remove heavy metals like precipitation, biosorption to cell walls, transport across the cell membrane, entrapment in extracellular capsules, oxidation/reduction, and complexation [107]. Bacteria species such as *Bacillus sp*, *Micrococcus luteus*, *Pseudomonas cepacia*, *Bacillus subtilis*, and *Streptomyces coelicolor* have been used by researchers for copper removal from wastewater [108,109].

Yeast is a fungus that has a larger size than bacteria and it has a nucleus and associated cytoplasmic organelles like other eukaryotic organisms. The cytoplasm present in the living cells is important to interact with metal ions and after entering into the cells, the heavy

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Table 9: Heavy metal removal using Algae.

	Biomass	Type of metal removed	Q (mg/g)	Reference
Algal	Sargassum sp.	Zinc	118	[95]
	Apanothece halophytic	Zinc	133	[96]
	Fucusvesiculosus	Lead	270	[97]
	Ascophyllumnodosum	Cadmium	215	[98]
	Macroalga, Sargassum Muticum	Copper	71	[99]
	Cystoseira Crinitophylla	Copper	160	[100]

Table 10: Heavy metal removal using Microbial biomass.

	Biomass	Type of metal removed	Q (mg/g)	Reference
Bacterial	Thiobacillusferroxidase	Chromium	82	[112]
	Bacillus firmus	Copper	381	[113]
	Streptomyces rimosus	Lead	135	[114]
	Pleurotussapidus	Lead	69.77	[115]
Fungal	Phanerochaetechrysosporium	Cadmium	127	[116]
	Penicilliumchrysogenum	Lead	116	[117]
Yeast	Baker's yeast	Copper	65	[118]
	Saccharomyces cerevisiae yeast	Copper	9.01	[119]
	Saccharomyces cerevisiae biomass	Copper	2.59	[120]

metal ions are separated into compartments for removal [110]. Researcher shows that the brewing industry by-product waste beer yeast is a cheap and promising adsorbent for copper removal from wastewater [111]. The following table show adsorption capacities of Microbial biomass (bacteria, fungi, and yeast) on different types of heavy metals [112-120] (Table 10).

Membrane Bioreactor (MBR) is an optional way to apply water reuse applications in wastewater treatment Because of its quality, compact size, removal efficiency, and the least amount of daily waste activated sludge. Fouling in the membrane is a major difficulty that significantly increases the maintenance and operation costs and also, deposition of the cell on the membrane, exertion of Extracellular Polymeric Substance (EPS), and Soluble Microbial Products (SMP) cause severe biofouling [121].

Nitrification is an aerobic process that is performed by nitrifying bacteria by comparing with heterotrophs released different metabolites in the activated sludge. During Aerobic heterotrophic metabolism, large amount of waste activated sludge are produced and the activity of *Nitrosomonas* and Nitrobacteria are prevented by accumulation of heterotrophic bacteria and their waste. Heterotrophs assimilate ammonia and consume oxygen before reaching nitrifies. Nitrifies outcompeted by heterotrophic bacteria because of the presence of high amount of organic loading rates [121].

Nitrification is the most known reaction of Alkanity consumption and also in fact that for nitrify growth and activity. Alkalinity is used to supply the appropriate abiotic factors. The shortage of foulding and alkalinity are two different problems that lately make microorganism de activated. So, the removal of foulding is much harder and time consuming than alkanity supply for the microorganism. waste water containing low C/N ratio the A Nitrifying-Enriched Activated Sludge (NAS) approach low foulding and increasing the preparation in 2.5 times higher than Conventional Activated Sludge (CAS) and reducing in microbial product in NAS had different fulfill the result [121].

A unique strategy for nutrient recycling manifested by the symbiotic algae bacteria and also the removal of contaminant in municipal and industrial water treatment. Algae produce oxygen which used as election accepted by aerobic bacteria, this stimulating the biodegradation of the substrate through by oxygenic photosynthesis. Algae have a networking potential for competing microbial species such as pathogens, and also the improvement of the dissolved oxygen concentration, PH, and temperature. Different

unicellular micro algae including *chlamydonas*, *chlorella*, *vulgaris* and *phormidium* have been used for algae bacteria culture. Algae is used for govern the consumption of CO_2 and also to provide safe and cost effective alternative to mechanical aeration. Removal of nitrogen and phosphorous need using more than 90% of could achieve 5:1 (algae/sludge, w/w) culture and also in the conventional activated sludge process a high organic loading rate cause higher amount of sludge production [122].

The result of ammonium removal is scarcely distinguishable from those who investigated inoculation ratios. The concentration of nitrite in nitrite community follows a boom and bust test and famine) cycle. When *C.vulgaris* proposition increase the nitrify actively was decrease because of it is lower weight percentage increase the assimilation and carbon capture activity of *C.vulgaris*. Phosphate is used for the sustainable growth of *C.vulgaris* and luck of phosphate compounds in media leads to the suppression of photo synthesis. Conversion of CO_2 in to other soluble carbon is one of main part of carbon cycle and also carbon dioxide [122].

Sequestration is the chemistry of CO_2 after being dissolved in water is completely dependent on PH via the equilibrium reaction. The inorganic carbon demand increased from B 10 to B 90 through the nitrification activity of nitrifiers and the higher assimilation. In this study *Chlorella vulgaris* and NAS by conduct to examine the removal of generation and also to the removal of ammonia. B 10 requiring 7 days as the other composition greater than 14 days the maximum p removal achieve B100 [122].

In the culture and organic metabolite generation, the analysis of EPS and SMP demonstrated a positive relation between the proportion of *C.vulgaris* and also membrane bio reaction can remove nutrients more efficiently and it could influence the interaction the *C.vulgaris* - NAS culture. Various carcinogenic or genotoxic by product such as trihalomethane is formed when chlorine reacts with EPS and SMP in effluents [122].

Clay minerals: Clay is a type of small particle found naturally on or near some planetary surfaces. water, alumina, silica, and weathered rocks are the main components of clay [123]. The basic structure of clay minerals consist of repeating units of Si-O tetrahedral (T) and Al-O octahedral (O) that form layers or sheets that bind together by sharing oxygens as shown in figure 2 [124,125]. Clay minerals characterized

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by layered structural units made up of one or two tetrahedral silica sheets around an octahedral arrangement consist of Fe, Mg, or Al atoms surrounded by six hydroxyl or oxygen atoms aluminum sheet [126]. Clays have different physical properties like hardness, fineness of particles, good plasticity, appropriate shrinkage, associativity high refractoriness, and surface decoration [127]. Clays have a complex porous structure such as small particle sizes and high specific surface area and this leads to facilitate physical and chemical interactions with dissolved material. Crystallinity, electrostatic repulsion, adsorption, and some cation exchange reactions are causes for the interaction [127] (Figure 5).

There are three main groups of clays called kaolinite, bentonites, and mica [18].

Kaolin group: Minerals are one of the most common clay forms in warm and humid climate [128]. It has a 1:1 layered structure which comprised a tetrahedral SiO_4 sheet and an octahedral sheet. Kaolinite application in water purification is growing rapidly with the conjunction of other clay minerals and H^+ ion promotes the adsorption of heavy metal ions which is released from the edge of the layer structure in acidic environments, like lead, copper, mercury, and cadmium from aqueous solution [129].

Bentonite: Is a kind of sedimentary rock comprised largely from clays that have a typical 2:1 layer structure and of Na^+, Ca_2^+, and Li-ions located between the layers in high concentrations. The octahedral and tetrahedral sheets are in such a pattern that the tips of the tetrahedral in each silica sheet and one of the hydroxyl layers in the octahedral sheet constitute a single layer. Due to the constant expansion of the layers, the distance between the 2:1 layers is not determined. Among other types of clay minerals bentonites mainly montmorillonite possess the greatest cation exchange capacity. It takes much attention due to its highly selective and regenerable and found to be cheaper as compared to Activated Carbons [130].

Mica group: Have also 2:1 layer however the isomorphic substitution occurs in the tetrahedral layer by mica group clay minerals where Si^{4+} is replaced by Al^{3+}. Common mica group minerals consist of phlogopite, muscovite, and biotite. Most natural illites are mixed layers of muscovite-like minerals and smectite-like minerals also mica groups are commonly known as illite [131]. Illites make up the bulk of ancient shales, and illitization reactions are common during late diagenesis of siliciclastic materials [132-145] (Table 11).
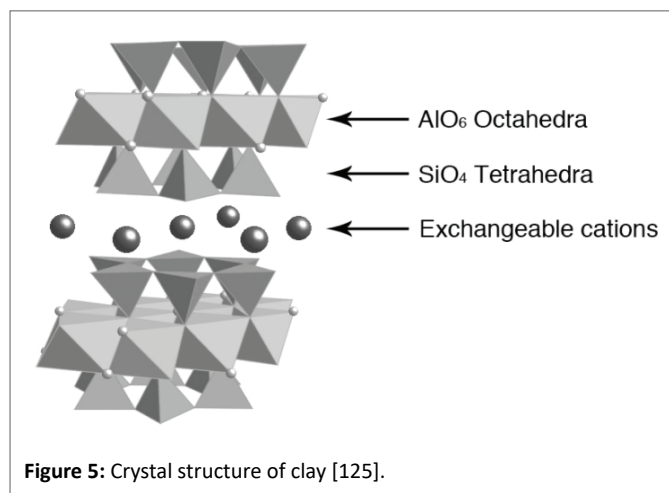
Figure 5: Crystal structure of clay [125].

Zeolite: Zeolites are among the best adsorbents because they are composed of three-dimensional crystalline, hydrated aluminosilicates made from the interlinked tetrahedra of silica $[SiO_4]^{4-}$ and alumina $[AlO_4]^5$. The two major characteristics of the open tetrahedral framework of zeolites are Ion exchange and reversible dehydration [146]. Zeolites have much scientific and industrial significance because of their good ion exchange properties, high surface area, nontoxicity, low cost, abundance, and hydrophilic characteristics. Due to those characteristic zeolites are applicable in many areas like drying, purification, water softening, environmental treatment, radioactive waste storage, catalytic activities, and so on. Zeolites are mostly applicable in the cause of water treatment due to their satisfactory potential for removal of metal ions from solution [6,147] (Figure 6).

Based on their pore size Porous materials are classified into microporous and mesoporous materials. Materials with pore diameter from 20 to 500Å are known as Mesoporous materials. They have large surface areas and provide many numbers of sites where sorption processes can occur. So those materials have certain applications in catalysis, separation, and many other fields. From reported materials, some kinds of silica and alumina, mesoporous oxides of cerium, niobium, tantalum, titanium, tin, and zirconium are the most known mesoporous materials. Materials with pore diameters of less than 2 nm called Microporous. These materials are mainly used in the laboratory to facilitate the contaminant-free exchange of gases, bacteria, and other contaminants so they allow the sterile environment in the contained area. Zeolites are also known members of this family [148-150].

Zeolite occurs naturally [151] but is also can be synthesized [152]. Zeolite can be classified as natural zeolite and synthetic zeolite based on the source in which they occur. Both natural and synthetic forms of zeolite is available in commercial quantity. The variable phase purity of the natural zeolite and the chemical impurities make a difference between the natural and the synthetic zeolite. Both natural and synthetic zeolites are used for different applications [152].

Natural Zeolite: Natural zeolite is a naturally occurring zeolite that was first discovered by a Swedish mineralogist Freiherr Axel

Table 11: Heavy metal removal using clay mineral.

	Type of metal removed	Q (mg/g)	Reference
Kaolin	Cadmium	41.84	[133]
	Copper	10.78	[134]
	Cobalt	11	[135]
	Nickel	140.84	[136]
	Zinc	4.95	[137]
Bentonite	Cadmium	11.2	[138]
	Copper	17.87	[139]
	Cobalt	0.91	[140]
	Nickel	92.59	[141]
	Zinc	8.21	[142]
Mica	Cadmium	22.17	[143]
	Copper	42.43	[143]
	Nickel	6.68	[144]
	Zinc	98.04	[145]

Figure 6: Crystal structure of zeolite [148].

Surface activity exists in this material take a great appreciation because the material shows superficial interacting with large organic molecules, charge exchange capacity, and polar adsorption [155]. Nowadays the application of natural zeolites is limited due to more interesting properties of synthetic zeolite such as greater thermal stability as well as good properties as specific catalysts. Synthetic zeolite gets more interest than natural zeolites due to the coast purification method as variable phases and chemical impurities. Contrarily at a time where uniformity and purity are not useful natural zeolite may get favor due to its cheapness [152].

Synthetic Zeolite : The idea of Zeolite synthesis was originated by Richard Barrer and Robert Milton in the 1940s. during 1940-1950 synthesis of zeolite A, X and Y open a way to introduce the idea of industrial adsorbents class in 1954, and after discovering the final structures of zeolite-A and zeolite-X in 1959 they come by the name hydrocarbon conversion catalysts [161].

Synthetic zeolites are also called molecular sieves which are crystalline aluminosilicates manufactured by heat. Zeolites identify as minerals of natural origin however recently more than one hundred different types of zeolite are synthesis [162]. Zeolite was formed when a reaction occurs between volcanic ash and water of basic lakes by taking several thousands of years. However, in laboratory conditions, it takes a short parried of time and can be made by hydrothermal processes from natural raw materials or synthetic silicates [162].

Zeolites where generally, the non-framework cations are replaceable and the molecules of waters are also removable and they could found several elements in the pores of synthesized zeolites; metal-silicates and microporous alumina phosphate was included in classes of molecular sieves [161]. While the aperture extent or the planar range within a crystal is smaller than 20 Å it is determined as microporous and shows porosity or compactness.

Several types of zeolite by using SiO_2 either lower or higher than the natural zeolite in the same framework type. Stronger-acid catalytic activity, hydrothermal stability, and high hydrophobicity are the characteristics of adsorbent with high SiO_2. Opposing this lower SiO_2 leads to greater cation exchange capability with higher absorbance for polar molecules. Sometimes elements like Ga^{3+} or $Ge4+$ have been substituting Al^{3+} and Si^{4+} partially or wholly in some cases, this strong element replacement gives more definite substitutional disorders on the information. Many sources such as coal ash, SCBA, and rice husk ash were used to prepare synthesized zeolites [163-166]. There are two groups to synthesize crystalline materials which are solid-state reaction and liquid phase reaction. In the cause of solid-state reaction the temperature used is above 300°C to overcome difficulties

Fredrick Cronsted, during the collection of minerals in a copper mine. The new mineral called zeolite because of its characteristic observed by crested during blowpipe tests on the new crystals he invents. Zeolite is derived from two Greek words "zeo" to boil and "lithos" a stone. Since the first zeolite discovered by crusted approximately 50 natural zeolites have been detected. These minerals were known before constant recognition of it as a distinct mineralogical species. The minerals were used as dimension stones in the construction of pyramids and also as temples in Mexico, in Cappadoccia used they built houses and churches Romans also used it for the production of pozzolanic cement. Hunters and geologists realized crystals of different zeolites in the cavities of basaltic and volcanic rocks.

However major geological discoveries have revealed the widespread occurrence of natural zeolites after 1950. Since the beginning of the last century Natural zeolites whose origin is sedimentary were used for different applications in different areas of environmental protection. These applications are due to important properties exhibited in these materials, such as cation exchange, alkali metals reactivity, physical adsorption and expansion tendency, thermal insulation, compressive strength, and durability [153-155].

Some Countries have resources of these minerals and production potentials such as Cuba, the USA, Russia, Japan, Italy, South Africa, Hungary, Bulgaria, and Turkey have substantial zeolite resources. there are no certain figures determined in the world amount of zeolites but it is well known that even the mineral contents and kind vary they are available on all the continents [156].

Natural zeolites subdivide into several subgroups based on their structures some of them are:- Natrolite which is a fundamental chain-like unit, Harm tome the chains are linked laterally and contain four and eightfold rings, Chabazite the structure exist single or double six-fold rings of tetrahedral, Faujasi tetetrahedra form pseudocubic symmetry form due to joined Cubo octahedral cage-like units. Modernite containing five-fold rings of Tetrahedral which can be linked in various ways and Heulandite [157-160] (Table 12).

Table 12: Heavy metal removal using natural zeolite.

S/N	Raw materials	Type of metal removed	Q (mg/g)	Reference
1	Natural mordenite	Chromium	3.5	[158]
2	Natural scolecite	Chromium	14.5	[158]
3	Clinoptilolite	Chromium	4.1	[159]
4	Clinoptilolite	Lead	78.7	[159]
5	Bentonite	Cadmium	9.44	[160]
6	Na-clinoptilolite	Copper	4.8	[160]
7	Na-clinoptilolite	Lead	91.2	[160]

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in the transportation of molecules while for liquid phase reaction the transportation of molecule is easier because the presence of solvents so the synthesis process is done at low temperature. There are three methods for Zeolite syntheses in the liquid phase are Hydrothermal method, Solvothermal method, and Ionothermal methods [167].

Comparison of several adsorbents based on the adsorption efficiency of metals. As we discuss above different adsorbents have various efficiency as well they have a different response for various metals. This can be summarizing in the table below [168-177] (Table 13 and 14).

Nanostructured materials

Nanostructured Materials are materials with a microstructure whose structural elements, clusters, crystallites, or molecules have dimensions of 1 to 100 nm range. A collection of distinguishable units in which the units are made of a limited number of atoms are Nano-sized material. Their fundamental electrical, optical, and magnetic properties lead to a great interest in both academic and industrial levels over the past decade [178]. The properties of Nanostructured Materials differ from those of bulk materials with the same average chemical composition. This difference results from the reduced size and dimensionality of the Nano-sized materials. Nanomaterials properties make them deviate from the bulk materials, including high surface energy, a large fraction of surface atoms, reduced imperfections, and spatial confinement [179].

Table 13: Heavy metal removal using synthetic zeolite.

S/N	Raw materials	Type of metal removed	Q (mg/g)	Reference
1	Synthetic zeolite A	Cadmium	315.65	[168]
2	Zeolite from fly ash	Cadmium	195	[169]
3	Zeolite X	Cadmium	92	[170]
4	Zeolite A	Copper	41.6	[160]
5	Zeolite X	Zinc	41	[170]
6	Zeolite A	Nickel	24.65	[160]
7	Zeolite A	Lead	213	[160]

Table 14: Heavy metal removal using various adsorbent.

S/N	Type of materials	Type of metal removed	Efficiency (%)	Reference
1	Graphene oxide	chromium	92.65%	[171]
2	activated carbon	chromium	84.8%	[172]
3	Clay	Lead	88%	[173]
4	Activated carbon from olive stones	cadmium	23%	[34]
5	Eggshell	chromium	93%	[65]
6	Bottom ash	cadmium	72.47%	[174]
7	Fly ash Modified by Acetic acid	Copper	60.07 %	[175]
8	Zeolite from fly ash	Cadmium and zinc	95.6%	[169]
9	Natural Zeolite	Copper	99.86%	[176]
10	synthesis zeolite using Silica Gel	Lead	91.86	[177]

The methods that are listed above which are Conventional materials have limitations of adsorption capacity and do not provide the desired removal efficiency for most treatments of heavy metals from wastewater due to the reason scientists perform research's to develop novel adsorbent with the best characteristic [180]. Nanomaterials are adsorbents that efficiently remove heavy metals from wastewater due to their enhanced active sites, high surface area, and the functional groups on their surface [181]. Certain areas including the removal of heavy metals from wastewater apply Nanomaterials because of their unique physical, chemical, and mechanical properties. Besides their high specific surface, these materials have very high strength, electrical conductivity, resistance, and thermal stability therefore they are used as effective adsorbents.

Types of nanoparticles: There are few naturally formed nanomaterials are occur which are from different bacteria types, volcanic eruptions, cosmic dust, and so on. Many man-made nanomaterials include fullerenes, graphene, carbon nanotubes, metal oxide nanorods, quantum dots, etc. [182]. There are different classes of Nanoparticles due to morphology, size, physical properties, and chemical properties. Some of them are carbon-based nanoparticles, metal nanoparticles, ceramic nanoparticles, semiconductor nanoparticles, polymeric nanoparticles, and lipid-based nanoparticles [179]. In this review paper, we will see only carbon-based nanoparticles and metal nanoparticles which are usually used in the adsorption of heavy metals from wastewater.

Carbon-based nanoparticles: Carbon-based nanoparticles include fullerenes, graphene, and carbon nanotubes.

Fullerenes: - Fullerenes are the allotropes of carbon represent closed cage of carbon molecules and the carbon units in these structures have a pentagonal and hexagonal arrangement. They were discovered in 1985 through spectrometric measurements its looks like hollow football and the structure of C-60 is called Buckminsterfullerene. their electrical conductivity, structure, high strength, and electron affinity lead them to have many commercial applications[183].

Fullerene's large specific surface area and the low tendency for aggregation make it interesting to apply them as adsorbents for the treatment of wastewater from the industry's [184]. These materials also extract different species from water because of its hydrophobic surface, high electron affinity, and high surface to volume ratio [185].

Graphene: - Graphene is a carbon-based is a two-dimensional, atomic-scale made from carbon atoms which were first invented in 2004. Like CNTs, it also has unique structural, mechanical, physical, and chemical properties that allow it to use in different fields [186].

Pristine graphene, graphene oxide, and reduced graphene oxide are the various forms in which graphene's available. To add hydrophilic groups for the removal of heavy metals graphene may be oxidized [187].

Recently the application of graphene and graphene-based materials is rapidly growing for environmental purposes including wastewater treatment because of their properties like enhanced active sites, high specific surface area, and the functional groups, and good chemical stability [181]. Researchers also confirmed that these materials have high sorption activity for the removal of heavy metals [188,189].

Carbon nanotubes: - Carbon nanotubes are graphene sheets rolled into a tube they are 100 times stronger than steel so they are mainly used for structural reinforcement. these materials were invented in 1991 [190]. These materials are classified into single-walled carbon nanotubes and multi-walled carbon nanotubes [179]. Carbon

nanotubes have a unique structure, semiconductor, mechanical, chemical electronic, optoelectronic, and physical properties which led research into a new area. They are efficient adsorbents for heavy metals due to the above properties combined with chemical stability, large specific surface area which is larger than fullerenes, and availability of well-developed mesoporous [191].

Metal nanoparticles: Metal nanoparticles are produced from metal precursors by chemical, electrochemical, or photochemical methods either from pure metals like silver, gold, platinum, iron, zinc, cerium, titanium, or their compounds such as oxides, hydroxides, phosphates, fluorides chlorides, and sulfides. Metal nanoparticles can adsorb small molecules so they are applicable in different research areas [179].

Metal Oxide nanoparticles: Metal elements can make a variety of compounds of oxides that can be used in different areas such as physics, chemistry, and material science. The goal in nanotechnology fields is to make nanomaterials with the special property which can adopt a variety of structural geometries with an electronic structure that can exhibit metallic, semiconductor, or insulator character. Due to their small size and high density of edge surfaces oxide nanoparticles have a unique physical and chemical property [192].

Properties of Metal Oxide nanoparticles: The physicochemical properties of nanomaterials are depending on their size which has special uses in chemistry. Many applications use nanomaterials directly related to their size dependence of oxide nanomaterials properties like mechanical, transport, electrical, optical, and surface chemistry [192].

Mechanical properties: - Low yield stress, hardness, and high super plasticity are the main concerns in mechanical properties. The mainly analyzed parameters are ductility, and super plasticity due to the lack of information Information on oxide nanomaterials [192].

Transport properties: - Metal oxide materials exhibit ionic or mixed ionic electronic conductivity. Both can affect by the nanostructure of the oxide this was experimentally defined and Boltzmann statics proposed that the number of electronic charge carriers is a function of bandgap energy [192].

Optical properties: - it is one of the most fundamental properties of metal oxides which can be obtained by reflectivity and absorption measurements experimentally [192].

Chemical properties: - In redox and acid/base properties oxides are essential for Absorption and Catalysis. There are three key important features for the application of absorbents the coordination environment of surface atoms, the redox properties, and the oxidation state at surface layers [192].

Among several metal oxide nanoparticles, some oxides classify as desirable materials for adsorption of heavy metals some of them are iron oxide, copper oxide, titanium oxide, magnesium oxide, cesium oxide, alumina oxide, and zinc oxide. The interesting and promising uses of the materials are due to their high selectivity and capacity to remove heavy metals from wastewater beside this property their size also helps them to penetrate the contamination zone were bulk materials cannot [193].

Opposing the whole advantages of metal oxide nanoparticles there is a problem reported due to the size reduction of metal oxides. The decrease in the size of metal oxide leads to poor stability because of the increase in surface energy [193]. The poor stability of particles leads to agglomeration due to Van der Waals forces or other interaction so the surface area would decrease thus high selectivity and efficiency to

remove impurities will also decrease not only this the material may lose its mechanical strength [194-199] (Table 15).

Scientists have been work to improve the uses of metal oxide nanoparticles for removal of heavy metals from water and they suggest using those materials by emerging with other porous materials as a stabilizer or supporter to form nanocomposite adsorbent this overcome the limitations on the application of metallic oxide nanoparticles [193].

Composite materials

A material that is made up of two or more constituent materials with different chemical and physical properties then combined to make a single material that is varying from the individual material in the property. The use of metal oxide nanoparticles in water treatment is improved by combined using of the materials with alternative materials to overcome the limitations of those particles by using porous support materials as a matrix [200].

There are various matrixes which are used as a supporter for metal oxide nanomaterials but among those matrixes, zeolite is considered the best host and stabilizer because of its large surface area, hydrophilic, high ion exchange capacity, high thermal stability, tunable chemical properties, pores with 1.3 nm diameter, eco-friendly nature and inexpensive nature [193, 201]. Zeolite/Zinc Oxide Nanocomposite (Zeolite/ZnO NCs) was successfully synthesized by using a co-precipitation method for adsorption of Lead and Arsenic and get high adsorption capacity [193] and also magnetic nanocomposite of Fe_3O_4/zeolite/cellulose nanofibers were synthesized for removal of zinc from water and the result shows the highest efficiency [202].

Parameters affecting the adsorption process

The efficiency of adsorbent in water purification is affected by many factors such as Ph. Effect of agitation speed Value, temperature, the surface area of adsorbent, contact time, adsorbent dose, and initial concentration of impurity. The percent to remove heavy metals from aqueous solution is increased by increasing those factors that are listed above [193,202-206] (Table 16).

Initial concentration of impurity

As the initial concentration of heavy metals increases the adsorbed heavy metals are increased due to the formation of gradient concentration between aqueous solution and adsorbent surface this render to effective interaction of adsorbent and impurity [202,207]. This phenomenon is shown in the graph below for the removal of lead and arsenic as the concentration increases the adsorption capacity also increases [208] (Figure 7).

Table 15: Heavy metal removal using metal oxide nanoparticles.

S/N	Raw materials	Type of metal removed	Q (mg/g)	Reference
1	ZnO	Lead	6.7	[195]
2	TiO_2	Zinc Cadmium	15.3 7.9	[196]
3	$\alpha\text{-}Fe_2O_3$	Copper	84.46	[197]
4	$\gamma\text{-}Al_2O_3$	Nickel	176.1	[198]
5	$\alpha\text{-}FeOOH$	Copper	149.25	[197]
6	CeO_2	Chromium	121.95	[199]

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Other publication also shows the increase in adsorption capacity because more metal ion can be absorbed as the initial concentration of metal increases [209]. The study was conducted on the removal of Zn^{+2} and the obtained result for the initial concentration of zinc is almost the same that we have seen before the only difference here is it reaches a maximum at 3 ppm (Figure 8).

Contact time

Adsorption efficiency is rapidly increased at the first in the adsorption process and then a slow improvement occurs at a constant rate this is due to the empty adsorbent surface at the initial stage of the process so molecules adsorb rapidly. However, as time goes the adsorption process shows no change due to the saturation of the adsorbent surface. This effect can be elaborate by using some results obtained in different works [202,209] (Figure 9 and 10).

Effect of agitation speed

Adsorbent capacity firstly increased as the increased in agitation speed because at first the mass transfer of the adsorbate from the bulk solution to a hydrodynamic layer surrounding the adsorbent particles which result in greater efficiency and adsorbent capacity and then become constant because of the thickness of the hydrodynamic layer decreases to some degree [210]. Here we can

Table 16: Heavy metal removal using composite materials.

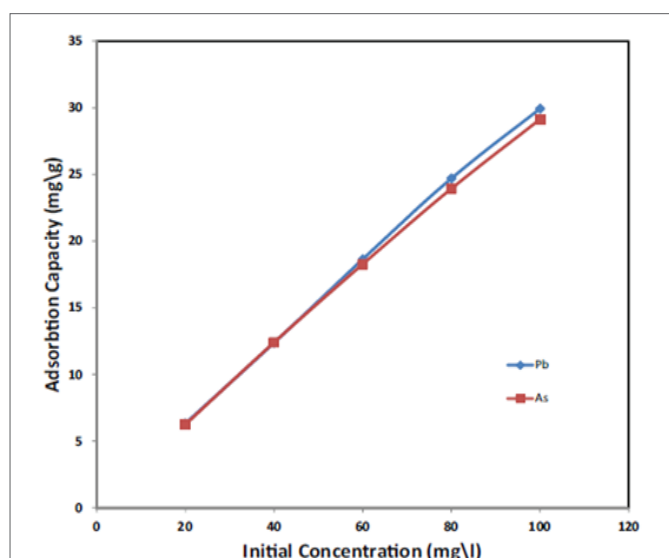| S/N	Raw materials	Type of metal removed	Q (mg/g)	Reference
1	G-MgAl-LDH	Chromium	172.55	[203]
2	GO-NH$_2$	Cobalt	116.35	[204]
3	SAGO aerogel	Lead	267.4	[205]
4	G-nZVI	Chromium	162	[206]
5	Fe$_3$O$_4$/zeolite/cellulose	Zinc	9.45	[171]
6	Zeolite and ZnO	Lead Arsenic	24.5 21.2	[162]

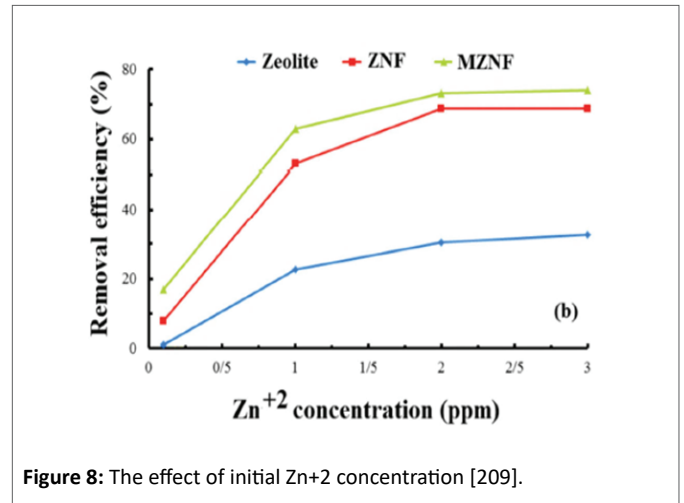Figure 7: Effect of initial Lead and Arsenic concentration on the adsorption capacity [208].

Figure 8: The effect of initial Zn+2 concentration [209].

see the published result which is conduct for removal of zinc ion from wastewater (Figure 11).

PH value

At low ph. value which is highly acidic hydrogen ion competes with metal ions to occupy the sites of the adsorbent [211] and also at high ph. the value which is a high alkali region there is the generation of more hydroxyl sites which also decreases the adsorption efficiency [212]. Better information can be obtained from the graphs below those results are conducted for different metals by different Nanocomposites (Figure 12 and 13).

Temperature

As many studies show that the efficiency adsorption process and temperature are proportional. As temperature increases the mobility of metal ions increases which increases the probability to find an empty site on the absorbent this leads to an increase in adsorption capacity. [202,213]. The effect of temperature on the removal efficiency of zinc ions is shown in the obtained result of the graph below (Figure 14).

Dosage of adsorbent

An increase in adsorption leads to an increase in adsorption capacity due to the larger surface area and more adsorption sites formation as a result more heavy metals can be attached to the adsorbent [214]. After reaching the maximum efficiency the removal efficiency will decrease due to aggregation of adsorbent which leads to a decrease in the surface is [215,216] a published result below shows the phenomena of adsorbent dosage on the efficiency of adsorption (Figure 15 and 16).

Specific surface area (SSA) of the adsorbent

The higher surface area formed a porous layer on the surface and in the channel of the adsorbent structural thus the adsorbent with a large surface area provides a large number of functional groups that enhance the adsorption process [217,218] (Figure 17 and 18).

In the study, the performance was assessed by comparisons on adsorption capacities of differently modified nanoparticles on different heavy metal ions (Cu, Cd, Co, Ni, Pb, As, Cr, Zn, Mn, and Hg). As shown in the above figure a general increase in adsorption capacity due to an increase in a specific area with the introduction of multi-functional group materials [219].
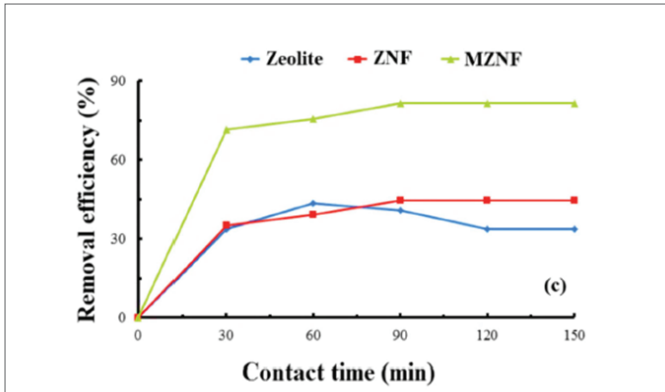
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Figure 9: The Effect of contact time on removal efficiency of zinc [209].

Figure 10: The Effect of contact time on the percentage of removal of lead and Arsenic [208].

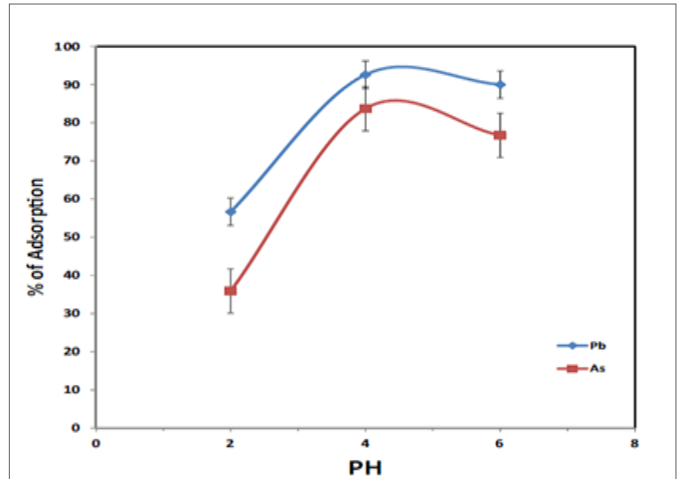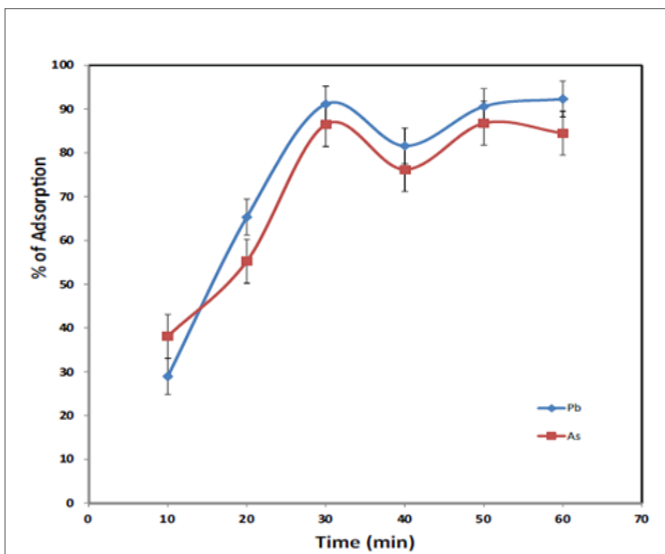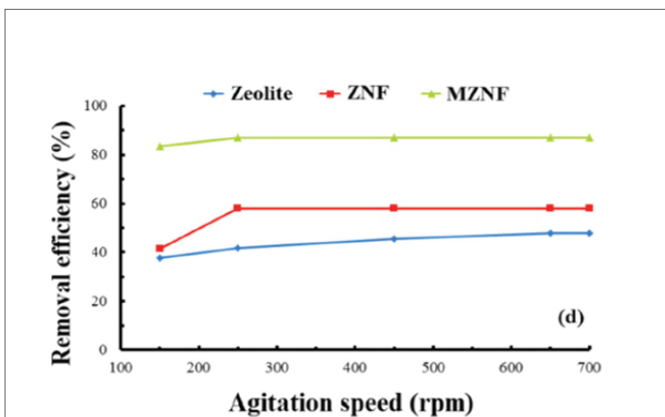**Figure 11:** The effect of agitation speed on the removal efficiency of Zn^{+2} ions [209].

Figure 12: Effect of pH solution on the percentage adsorption of lead and Arsenic [208].

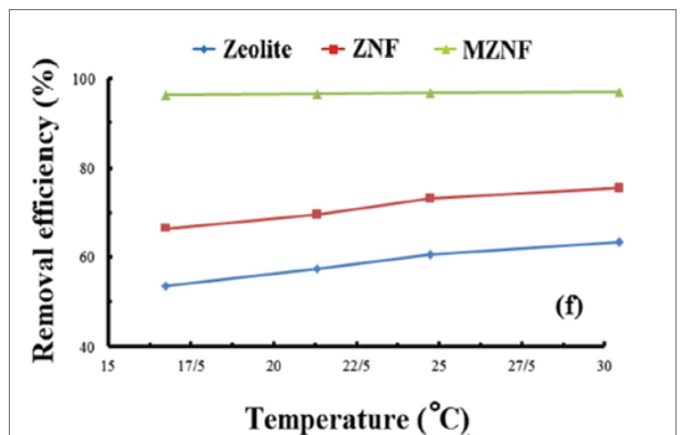**Figure 13:** The effect of pH on the removal efficiency of Zn+2 ions [209].

Figure 14: The effect of pH on the removal efficiency of Zn+2 ions [209].

Conclusion

In the recent paper, detailed information for conventional and nanostructured materials in adsorption was discussed. The main focus of the paper was to show promising adsorbents like zeolites, metal oxide nanoparticles, and composite materials in the adsorption process. In this regard, Nano based materials have a unique physical, chemical, and mechanical property which makes them promising adsorbents. In converse to those advantages, there is a problem of agglomeration as the size of the materials decreases to Nanosized level due to the poor stability of the particles. To overcome this barrier scientists start to use a porous material with a high surface area as a supporter and engaged them with the nanostructure materials and obtained a successful result that opens away for future researches. From several works that are conducted on this is some of them are reviewed in this review paper and show away to study more.
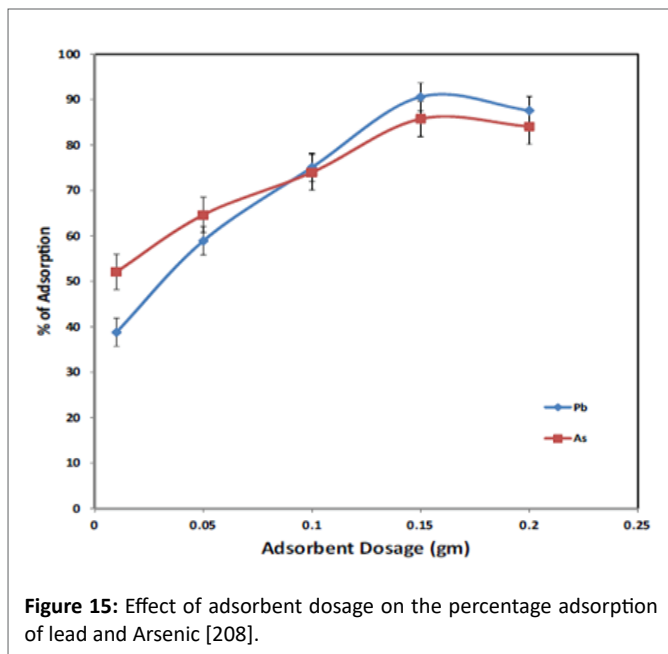

Figure 17: Comparison of adsorption capacities of naked and modified silica nanoparticles [219].

Figure 15: Effect of adsorbent dosage on the percentage adsorption of lead and Arsenic [208].

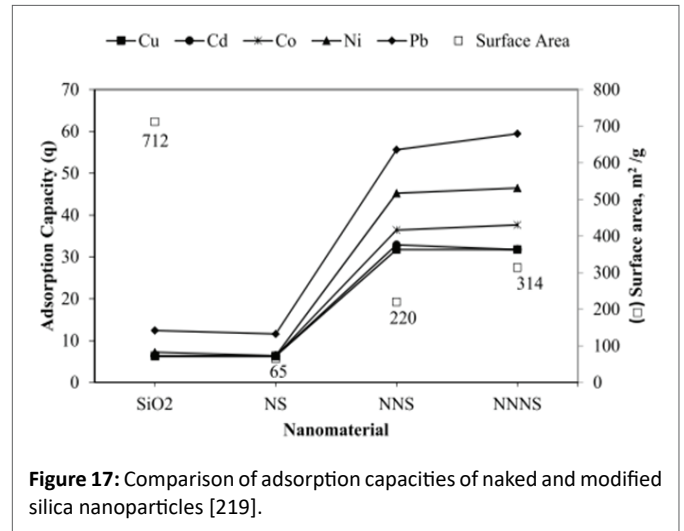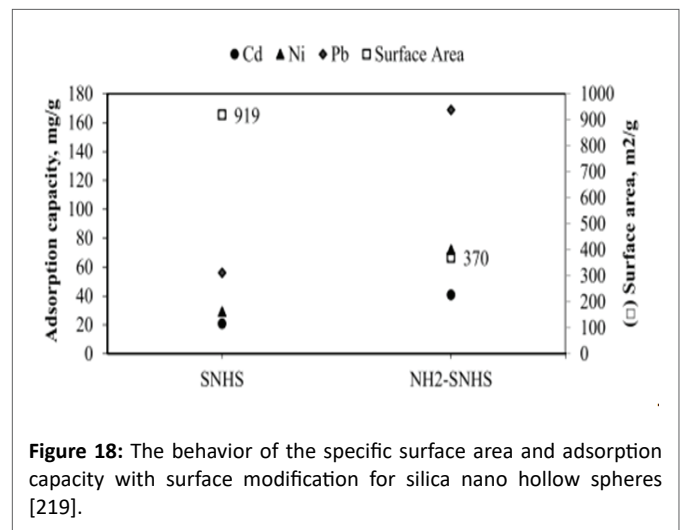**Figure 18:** The behavior of the specific surface area and adsorption capacity with surface modification for silica nano hollow spheres [219].

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Figure 16: The effect of adsorbent dosage on the removal efficiency of Zn+2 ions [209]

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