Biointerface Research in Applied Chemistry
Open-Access Journal (ISSN: 2069-5837)

Review
Volume 13, Issue 4, 2023, 397
https://doi.org/10.33263/BRIAC134.397

Comparative Review of Different Adsorption Techniques Used in Heavy Metals Removal in Water

Abderrahim Maftouh [1,*], Omkaltoume El Fatni [1], Souad El Hajjaji [2], Mohammad Wadah Jawish [3], Mika Sillanpää [4,5,6]

1 LPHE-Modeling & Simulations, Faculty of Sciences, Mohammed V University in Rabat, Rabat, Morocco; abderrahim_maftouh@um5.ac.ma/abderrahim.maftouh04@gmail.com (A.M.), o.elfatni@um5r.ac.ma (O.E.F.);
2 Laboratory of Spectroscopy, Molecular Modeling, Materials, Nanomaterials, Water and Environment, (LS3MN2E-CERNE2D), Chemistry Department, Faculty of Sciences, Mohammed V University in Rabat, Rabat, Morocco; s.elhajjaji@um5r.ac.ma (S.E.H.);
3 Chemistry Department, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia; mohammad.wadah3840@alum.kfupm.edu.sa (M.W.J.);
4 Faculty of Science and Technology, School of Applied Physics, University Kebangsaan Malaysia, Bangi, Selangor, Malaysia.
5 School of Chemistry, Shoolini University, Solan, Himachal Pradesh, India;
6 Department of Biological and Chemical Engineering, Aarhus University, Nørrebrogade, Denmark; mikaesillanpaa@gmail.com (M.S.);
* Correspondence: abderrahim_maftouh@um5.ac.ma (A.M.);

Scopus Author ID 57230346400

Received: 5.06.2022; Accepted: 30.07.2022; Published: 1.11.2022

Abstract: The rising shortage of water resources and the need to provide water in many regions like Morocco around the world has been crucial and will become increasingly alarming in the future. Water bodies can be practically polluted or impaired by industrial, agricultural, and anthropogenic waste. Heavy metals are widely known environmental contaminants due to their toxicity, prevalence, and bioaccumulation. They build up in the environment, disrupting the food chains as chronic pollutants. In organisms, including humans, the deposition of possibly hazardous heavy metals poses a significant threat to health. This review paper highlights the present research on heavy metal removal, focusing on adsorbents and techniques accessible and feasible, such as adsorptive separation by substances, including a metal oxide, graphene, zeolite, and carbon-based composites. These techniques received a lot of acknowledgment due to their significant active surface area, high proportion of functional groups, increased chemical and thermal stability, and impressive adsorption efficiency and efficacy. The economic aspects and feasibility of adsorbents have also been presented.

Keywords: anthropogenic waste; bioaccumulation; chronic pollutants; disrupting food chains; chemical and thermal stability.

© 2022 by the authors. This article is an open-access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

1. Introduction

Heavy metals include metallic substances with a higher density (4 ± 1 g/cm^3) than water, such as arsenic, which may cause toxicity even at low levels of exposure [1]. Heavy metal concentration in various bodies of water has become a significant concern lately because high concentration is hazardous to living creatures. Geogenic, industrial, commercial, pharmaceuticals, residential untreated sewage, and atmospheric sources have all been listed as heavy metal emitters in the environment and are the main sources that have been identified as anthropogenic sources of heavy metals [2,3]. In addition, metal corrosion, ozone accumulation, soil erosion, heavy metal liquidation, re-suspension of sediments, and metal evaporation from soil to water and groundwater may also cause environmental contamination [4].

Nickel, Copper, Cadmium, Zinc, Arsenic, and Lead are the most common heavy metals which are discharged from activities like smelting or treatment of metal ores, mines, burning of petroleum products from fossil fuels, unloading industrial waste, the disposal of household waste, food packaging, disposing of transportation vehicles exhaust gases, and the use of pesticides [5,6]. To prevent the physiological and ecological consequences of these metals' direct or indirect consumption, wastewater streams from these sources must be decontaminated before being discharged into rivers or ponds.

Table 1. Table showing Adverse Health Impacts of Heavy Metals**.**

Sr.	Heavy Metals	WHO Allowed Permissible Limits (mg/L)	Adverse Effects on Human Health
1.	Nickel (Ni)	0.07	Lung scarring, lung cancer, renal disease, and cardiovascular illness are all disorders that affect the lungs.
2.	Silver (Ag)	0.1	Argyriasis, liver and kidney dysfunction, and blood cell abnormalities.
3.	Iron (Fe)	3.0	At high amounts, hemochromatosis and liver cell destruction occur.
4.	Cadmium (Cd)	0.003	Acute toxic effects include headaches, osteomalacia, skin ulcers, eczema, vomiting, diarrhea, and malignancies.
5.	Arsenic (As)	0.05	Bronchitis, hyperkeratosis, cancer, ulcer, psoriasis, liver cirrhosis, and mental instability are all caused by it.
6.	Chromium (Cr)	0.05	All possible side effects are eczema, skin ulcers, reproductive infection, genotoxicity, embryotoxicity, and lung cancer.
7.	Cobalt (Co)	0.05	Allergic erythema, asthma, bronchitis, and carcinoma
8.	Lead (Pb)	0.05	Alzheimer's syndrome, senile impairment, kidney dysfunction, cancer and neurodegenerative disorders.
9.	Zinc (Zn)	3.0	Various cancers, neurological and respiratory diseases
10.	Mercury (Hg)	0.1	Gastrointestinal, inappropriate neurological development, and hypertension are among the side effects.

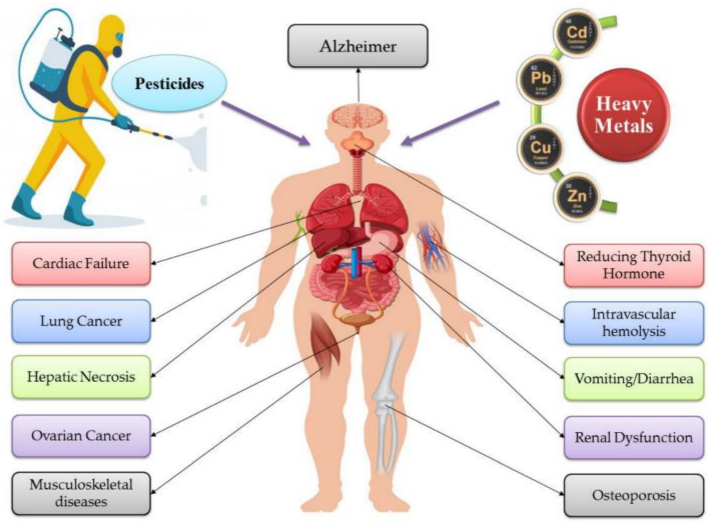

Figure 1. Impact of heavy metals on the human body [14].

Heavy metals each the human body through the skin, inhalation, or digestion and become hazardous whenever they are not metabolized by the body and consequently collect in soft tissues [5,7,8]. For example, chromium poisoning can result in liver, renal, cardiovascular, and neural disorders and skin irritation. Metals like cadmium and arsenic are known carcinogens that can cause skin, lung, liver, and bladder cancers. High mercury levels can permanently harm the neurological system and kidneys and impair infants' growth and brain function, leading to irritation, anxiety, tremors, visual or hearing impairments, and memory problems [9-13]. Table 1 depicts the maximum concentration of heavy metals that may be absorbed in the human body and the associated health conditions and disorders, while figure 1 represents various kinds of heavy metal poisoning and their potential hazards to human health.

Several recently reported articles demonstrated that treatment techniques and practices, such as membrane filtration, microbial bioremediation, advanced oxidation process (AOPs), carbon nanotechnology, electrochemical method, chemical precipitation, solvent evaporation, ion-exchange, photocatalytic, and biosorption are presently being evaluated for heavy metal removal from water in many developed nations [15-17]. However, in the setting of developing countries, these technological advances are neither viable nor cost-effective. To purify water in resource-limited countries, suggested technologies must be easily accessible, built by indigenous workers with minimum education, and have minimal running and maintenance expenses. Among the accessible methodologies, adsorptive separation by substances including a metal oxide, graphene, zeolite, and carbon-based composites has received a lot of acknowledgment due to their significant active increased chemical stability, increased surface area, a high fraction of functional groups, thermal stability, and impressive adsorption efficiency and efficacy [18]. Table 2 outlines the benefits and drawbacks of heavy metal removal methodologies.

Table 2. Table showing Benefits and Limitations of Heavy Metal Treatment Methodologies**.**

Sr.	Name of the Method	Benefits	Limitations
1.	**Coagulation and Flocculation**	High removal efficiency can be achieved with an adequate and appropriate chemical dose.	Physicochemical sludge formation that needs further treatment. Energy extensive. High operational costs
2.	**Ion exchange**	High cation and anion removal efficiency may be attained with the appropriate ion exchanger. It can also function successfully in low-pressure environments.	Because of the synthetic resin/beads, it is expensive. Resin is susceptible to oxidizing chemicals. The expenses of disposing of the acids and bases generated in regeneration
3.	**Membrane Filtration**	It can operate well even at low temperatures. There are no phase changes; both the feed and product streams remain liquid.	The technique is susceptible to membrane fouling, which results in a reduction in permeate flux. Expensive cleaning and regeneration processes are required. The high flow rates employed in cross-flow feed could degrade shear-sensitive materials.
4.	**Photocatalysis**	A less hazardous byproduct High photostability	Long processing time with less applicability
5.	**Chemical Precipitation**	There is a high degree of selectivity since highly specific components may be eliminated while leaving other substances unchanged.	High processing expenses will accompany the significant amount of salt generated.

This paper presents a comparative review of heavy metal removal techniques, focusing on adsorbents and accessible methodologies for the adsorptive separation of substances, including metal oxide, graphene, zeolite, and carbon-based composites. These methods have received a lot of acknowledgment due to their significant active surface area and a high proportion of functional groups, increased chemical and thermal stability, and impressive adsorption efficiency and efficacy. Considering the economic importance of treatment methodology to introduce it on commercial scale, this paper will also present an economic analysis and feasibility study of the most abundantly used adsorbent techniques to deal with heavy metal contamination.

2. Heavy Metal Adsorption Characteristics

Adsorption is a phenomenon that includes the deposition of a substance, in the molecular form, at a higher concentration on the surface. It depends on the existence of the adsorbent layer with a specific surface structure that can host a micro-substance on its surface [2,19]. Adsorption is considered an effective method due to its ability to remove even lower concentrations of heavy metals, low energy consumption, and availability of raw materials. Adsorption can be categorized into two major types: physisorption and chemisorption. Physisorption is a process in which absorbent and absorbate are attached by van der Waals forces, while in chemisorption, absorbate is attached to absorbent by making chemical bonds [20]. The three most crucial characteristics are functional groups on the surface, contact area, and ion exchange capacity that affect the efficiency of heavy metal deposition on a specific adsorbent media. The greater the surface area, the smaller the particle size, and the more available surface functional groups are, the greater the adsorption capacity [19,21]. Figure 2 represents the general flowsheet representation of adsorption, physisorption, and chemisorption.

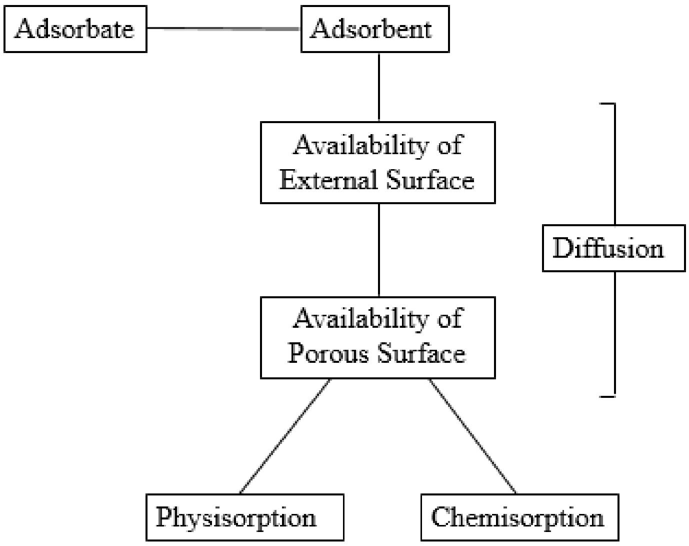

Figure 2. Schematic representation of adsorption pathway and techniques.

The underlying phenomenon of adsorption of heavy metals is complicated since it differs based on the adsorbent substances and the kind of heavy metal [22]. Figure 3 demonstrates the adsorption steps or process and how adsorbate and adsorbent interact throughout the separation process. For instance, heavy metals are adsorbing physically induced by the van der Waals forces that transpired between adsorbent heavy metal ions and surface macromolecules. Intermolecular interactions impact adsorption affinity, which is usually limited and may be reversible.

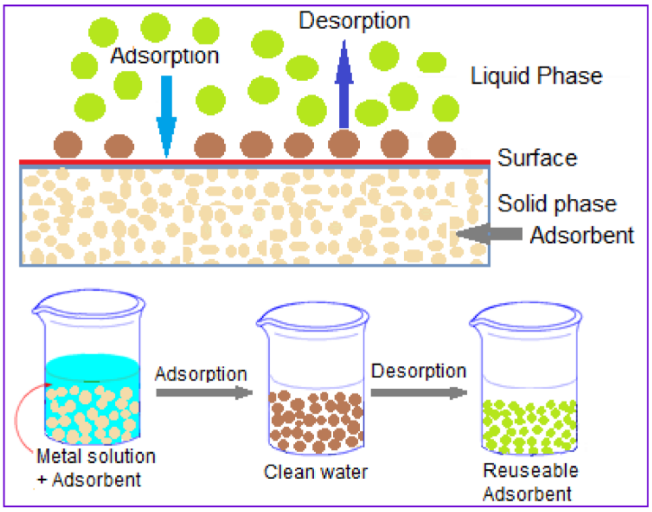

Figure 3. Adsorption and desorption process for heavy metal removal [23].

3. Reduction of Heavy Metals using Adsorption Mechanisms

Adsorption is an efficient reversible technique that can continue well even with diluted solutions of the adsorbate. The existence of narrow pores on the outermost surface of the sorptive component increases the adsorption efficiency compared to globular pores. The particles adsorbed onto the surface are concentrated and structured in a particular manner. Adsorption is affected by temperature, the type of adsorbent surface and adsorbate surface, the existence of additional contaminants, and ambient and experimental conditions (pH, pollutant concentrations, contact duration, and adsorbent particle size are all factors to consider). Moreover, because the performance of this method is harmed by the presence of suspended particles, oils, and greases, pre-filtration might well be required at times [24].

3.1. Reduction of heavy metals using activated carbon.

In many cases, activated carbon (AC) is used as an adsorbent in water treatment facilities for heavy metal adsorption due to its microporous structure, wide surface area, and chemical complexity. It has been demonstrated that reactive species on the surface and the pore size distribution affect the adsorption effectiveness of AC. The external surface contains a variety of functional groups, including phenol, carbonyl, lactone, carboxyl, quinone, and others. The tiny particle size, maximal interior surface area, and active free oxidation states of activated carbon contribute to its high adsorption potential. However, at temperatures around 300℃, AC could oxidize [25].

The high cost of coal-based AC stimulated more investigations on producing low-cost activated carbon from abundant and diverse agricultural waste products. One study investigated the effect of temperature, pH, contact time, and initial Cr^{+6} concentration on the performance of rubber-based products with sawdust mixture adsorbent [26]. Cr^{+6} can be extracted immediately by accessing the electron donor groups on the adsorbent and reducing the oxidation number from +6 to +3. Another method consists of three phases, beginning with Cr^{+6} binding to molecules on the interface of activated carbon that is positively charged. The next stage is for the electron donor groups adjacent to decrease to +3. Finally, due to repulsion between the ionic species and the positive charge regions, Cr^{+3} ions are released into the water. Adsorption generally depends on the adsorbent amount, temperature, duration, and solution pH (optimal pH of 12 was selected), and rice husk carbon has the highest Cr^{+4} absorption of 95%.

Therefore, another study used tartaric acid in addition to the standard rice husk adsorbents in batch investigations to modify rice husk-based AC, which were demonstrated to be promising Cu^{2+} and Pb^{2+} adsorption from aqueous medium using substances in the binary constituent [27].

The removal of Cd^{2+} and Zn^{2+} from nontreated water was investigated using AC produced from sugarcane bagasse. This AC had the highest absorption (100%) at pH 8.0, indicating a stronger selectivity than other adsorbents. It also investigated how to remove Cr^{4+} from heavy metal-contaminated water employing bagasse and coconut jute. The highest recovery rate was 99.8%, functioning best at low Cr^{4+} concentrations and pH values. The use of AC derived from coconut tree sawdust was investigated to remove Cr^{4+} from an aqueous medium [28]. Numerous adsorption investigations demonstrated that the maximum removal was obtained for particle sizes 125-250µm. The qmax calculated from the Langmuir adsorption isotherm was 3.46 mg/g at a starting pH of 3.0.

In another study, the remediation of heavy metals from the water was performed with the help of activated carbon from lignocellulosic biomass. The technique proved to be highly efficient as it was able to treat a wide variety of heavy metals, including Cr, Pb, Cu, Hg, Cd, and As. Results showed that the lignocellulosic biomass obtained from activated carbon is a highly eco-friendly and economical technique for dealing with water's heavy metal contamination. Figure 4 describes the process of heavy metal remediation using activated carbon [29]. Electrostatic forces involving heavy metal surface charge and AC are fundamentally separate adsorption processes influenced by ionic interaction charge. The intensity pH, the oxidation state of metallic ions, the electronic conductivity, and the zero possibility of activated carbon all influence electrostatic interactions [30,31].

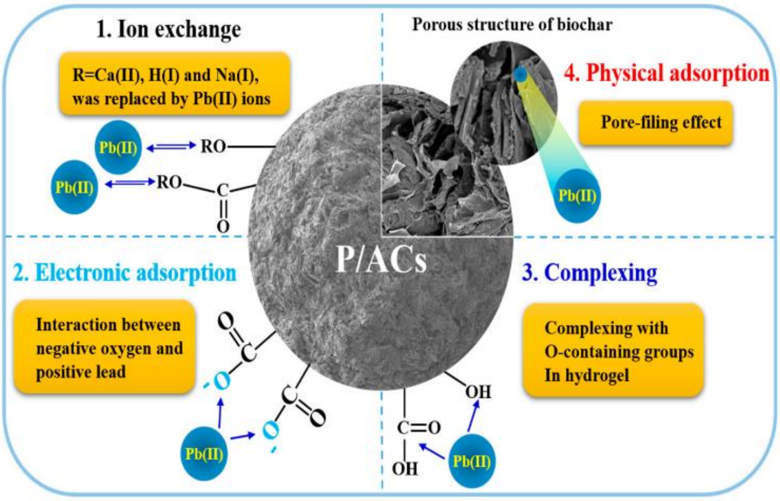

Figure 4. Adsorption of heavy metals by activated carbon [32].

3.2. Reduction of heavy metals using graphene.

Graphene is characterized by two-dimensional (2D) sp2 hybridization in a single layer, which makes hexagonal lattice formed through specific interactions of sigma and pi bonds among carbon atoms. Conventional graphene, graphene oxides (GO), and reduced graphene oxides (rGO)are some of the types accessible [33]. The distinctive mechanical, chemical and physical characteristics make graphene useful in reducing heavy metals from water. Its exceptional qualities consist of a sizable specified surface area, excellent chemical stability, and upgraded functional and active sites on its surface. Furthermore, the goal of creating a huge volume of graphene nanomaterials has been achieved using a cost-effective strategy for water purification. Since regeneration and recyclability of adsorbent is an important critical element for practical use of the adsorption process, several investigations have shown that a desorption procedure may be utilized to renew adsorbents based on graphene that employ either a strong acidic (HCl) or a strong alkali (NaOH) solutions [34,35]. Figure 5 shows the schematic illustration of the removal of heavy metals via graphene-based materials.

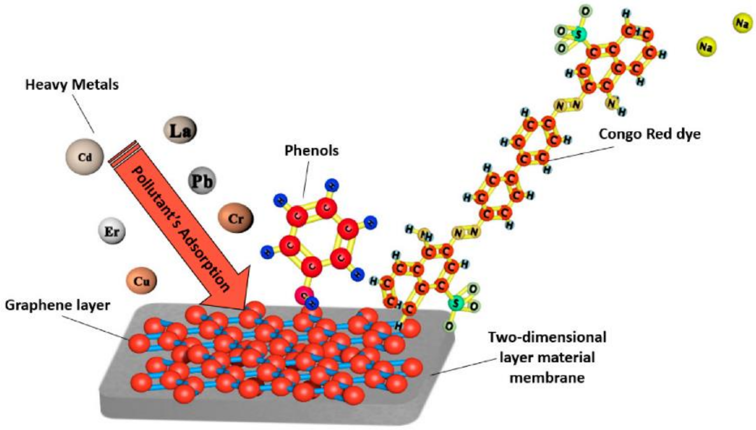

Figure 5. Removal of heavy metals, dyes, and Phenols by Graphene-based material [36]**.**

The oxidation of graphite generates GO, which is an oxidized variant of graphene. It has a significant negatively charged density and is hydrophilic due to the existence of oxygen-rich functional groups, and it is exceedingly robust due to its nonconductive nature [37]. One study used the electrolysis approach to generate functionalized graphene, which was then used as an adsorption process to remove Pb^{2+} and Cd^{2+} from wastewater [38]. The highest absorption capability was 406.6 mg/g for Pb^{2+} at pH 5.1 and 73.42 mg/g for Cd^{2+} at pH 6.2; both were attained within 40 minutes of equilibrium. Lignosulfonate-converted graphene gel has been advocated for an adsorption process due to its extremely pore structure, highly effective contact area, and adsorbed pores' interactions on the surfaces [39]. The modified Hummer's technique was used to investigate the adsorption of Pb^{2+} from wastewater using a few layers of GO from graphite. The presence of oxygen-containing functional groups on the adsorbent was found to increase the adsorption capacity to 1850 mg/g [40]. In another study, GO nanosheets synthesized with L-cystine, a naturally occurring and stable sulfur-containing amino acid, were utilized to extract and precipitate mercury (Hg) ions from aqueous solutions [41].

Table 3. Heavy Metal Remediation by using Graphene-based derivative material**.**

Graphene Type	Modification	Membrane Process Type	Heavy Metals	Removal Efficiency	Reference
Graphene Oxide (GO)	Metal – organic framework/grapheme oxide composite	Nanofiltration	Cu	~90%	[42]
Graphene Oxide (GO)	GO – isophorone disocyanate	Vacuum Filtration	Pb, Cu, Cd, Cr	40 – 70%	[43]
Graphene Oxide (GO)	Ceramic supported GO/Attapulgite composite	Vacuum Filtration	Cu, Ni, Pb, Cd	99%	[44]
Graphene Oxide (GO)	Carboxylated-GO incorporated polyphenylsulfone	Nanofiltration	As, Cr, Cd, Pb, Zn	98% (anions), 80% (cations)	[45]
Graphene Oxide (GO)	Fabricating GO/Torlon composite	Nanofiltration	Pb, Ni, Zn	95%	[46]
Graphene Oxide (GO)	GO framework by ethylenediamine	Nanofiltration	Mg, Pb, Ni, Cd, Zn	89%	[47]

Graphene Type	Modification	Membrane Process Type	Heavy Metals	Removal Efficiency	Reference
Graphene Oxide (GO)	Polyethersulfone nanofiltration membrane modified by magnetic GO/metformin hybrid	Nanofiltration	Cu	92%	[48]
Graphene Oxide (GO)	Graphene-based nanomaterials	Adsorption	Zn, Ni, Cr, Co	99%	[49]

3.3. Reduction of heavy metals using graphitic carbon nitride (g-C_3N_4).

Graphitic carbon nitride (g-C_3N_4) is an almost 2D nano-adsorbent and a relatively stable allotrope of carbon nitride. It features stacking of layer architectures and excellent thermal and chemical resistance under ambient environments.

The exterior amino groups of g- C_3N_4 is also significant in the adsorption of heavy metals, and it is expected to be a low-cost adsorbent for contaminants. Nevertheless, graphitic carbon nitride has received little attention for its potential applicability in the adsorption of heavy metals [50]. The ability of guanidine hydrochloride-based g- C_3N_4 to remove Cd^{+2}, Pb^{+2}, and Cr^{+4} from the water was tested. Elevated temperatures resulted in higher absorption capabilities, revealing the endothermic nature of g-C_3N_4 adsorption. It was found that Pb^{+2} and Cd^{+2} were predominantly adsorbed via electrostatic interactions on the tri-s-triazine units, while anionic Cr^{+4} was predominantly adsorbed on the g-C_3N_4 outermost layer. After ten regeneration cycles, 80% of the g-C_3N_4 adsorption capacity was still intact [51]. Figure 6 explains the advantages of graphitic carbon nitride (g-C_3N_4) in treating contaminated water.

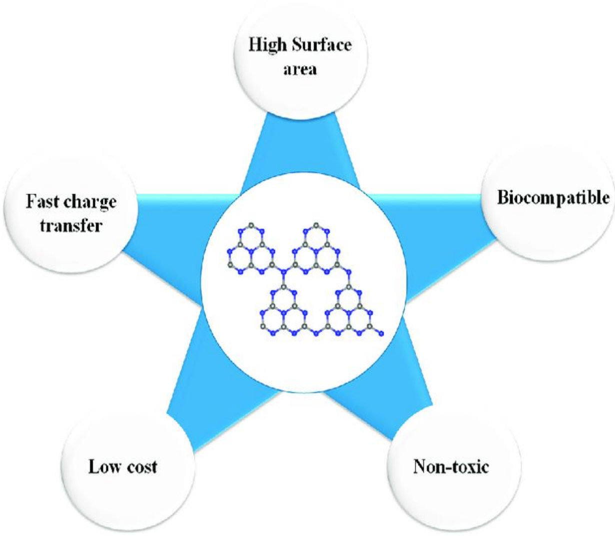

Figure 6. Advantages of Graphitic carbon nitride (g-C_3N_4) [52].

Shen *et al*. tested g-C_3N_4 to remove Cu^{2+}, Cd^{2+}, Pb^{2+}, and Ni^{2+} and found that the adsorption capability of g-C_3N_4 toward heavy metal ions was much more significant compared with activated carbon [53]. The association of the heavy metal ion with the carbon and nitrogen comprising functional groups of the adsorbent materials was described through the process of internal surface complex formation. Both graphene oxides and g-C_3N_4 demonstrated great sorption potential and exceptional regeneration potential, lowering the cost of the material properties and allowing them to be used efficiently in the treatment of wastewater contaminated with toxic material such as heavy metals[54]. The adsorption performance and metal ions capacity of g-C_3N_4 nanosheets produced using heat and ultrasonic methods have been found to be outstanding.

3.4. Reduction of heavy metals using carbon nanotubes (CNTs).

Significant development of Carbon nanotubes (CNTs) as outstanding adsorbents was achieved recently due to their extraordinary chemical and physical characteristics [55]. CNTs are long-lasting substances and generally poor adsorbents, but introducing additional functional groups to their outermost layer can significantly boost their sensitivity and capacity to capture heavy metals. In general, the surface of carbon nanotubes (CNTs) must be activated and functionalized with extra substances to render them more susceptible to various types of contaminants [56,57]. The most chemically activated carbon nanotubes have a variety of sites that are concentrated around substandard sections, such as pentagons, aligned against a tube body mostly made up of hexagons. It is possible that this gives CNTs a high capacity to connect with other chemicals [58]. The first step in increasing the efficacy of carbon nanotubes is to functionalize them. The optimal way to accomplish this is determined by the chemical and physical features of the CNTs in issue, namely their particle size, surface type, structure, and chemical compositions. Applying a functional group to the surfaces of carbon nanotubes is a necessary step in developing CNTs and boosting their unique properties [59].

Frayyeh *et al*. conducted a study by removing chromium II from contaminated wastewater with the help of specialized multi-walled carbon nanotubes. Results showed that the metal ion removal efficiency through CNTs was approximately 99% [60]. Another study on the usage of nanotubes for the removal of heavy metals showed that carbon nanotube absorbents show a high affinity for the removal of heavy metals. Studies exhibited that these CNTs tend to deal with a wider variety of heavy metals, such as Pb^{2+}, Cu^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, and Cr^{6+} [61]. The majority of heavy metals are adsorbed on the outer layer and interior sites of open-ended carbon nanotubes. The accessible surface area and surface functional groups are the primary drivers of this increased adsorption, and both factors have received considerable attention.

Nonetheless, the rate of CNTs' adsorption is determined by characteristics such as external surface area, pore density, functionality, and purity [62]. There are four key possible CNTs adsorption sites for heavy metals adsorption. There are interstitial channels (a), inner CNTs holes (b), grooves (c), and exterior CNTs surfaces (d) (Figure 7).

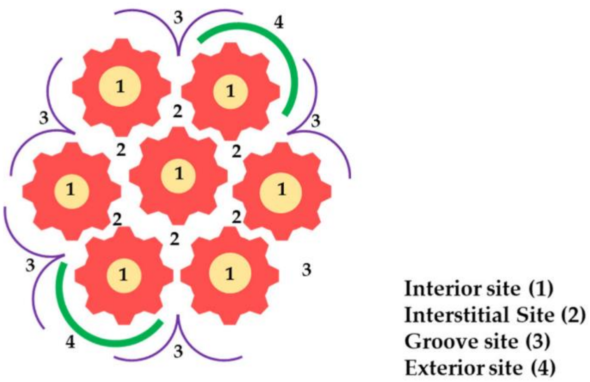

Figure 7. CNTs adsorption sites for heavy metals in water [63].

Depending on the shape of the nanotube, interstitial channels can act as a substantial trap for tiny pollutants. For example, single-walled carbon nanotubes (SWCNTs) create additional interstitial channels due to their aggregation effects—the aggregation rate decreases as the number of CNTs layers increases [64]. The pattern of CNTs aggregation is as follows: MWCNTs (Multi-walled carbon nanotubes) < DWCNTs (Double-walled carbon nanotubes) <

SWCNTs. CNTs aggregation can be advantageous or harmful to adsorption [65]. However, it diminishes the overall surface area of SWCNTs, which is required to adsorb heavy metals in bulk. It creates interstitial spaces between tubes, which increases the pore size (mostly MWCNTs) and enlarges the grooves in the outer spaces of the CNTs bundles. Because of their similar diameters, open-ended SWCNTs offer more versatility in adsorbing numerous adsorbents than MWCNTs. The adsorption effect of SWCNTs with lower diameters increases in the case of the occurrence of the chemical reaction between the size of the adsorbate and the diameter of the nanotubes. The CNT bundles' outermost surfaces and grooves have positive benefits for the adsorption of heavy metals [62,63].

3.4.1. Arsenic removal by using functionalized CNTs.

Previous research findings show that arsenic interacts with metal oxides with varying adsorbent bases. For example, an iron oxide-multiwalled carbon nanotube (Fe_2O_3-MWCNT) combination was effectively employed to remove arsenic As^{3+} and As^{5+} ions. At pH ranges of 7 – 8, the highest removal capacity was 84.8 percent, and Freundlich and Langmuir's adsorption models corresponded well with the results [66]. Table 4 lists the different functionalized carbon nanotubes (CNTs) utilized to remove arsenic and the observations made.

Table 4. Table showing functionalized CNT used for removal of arsenic.

Adsorbent Applied	Observations/Comments	Reference
Multi-walled carbon nanotubes (MWCNTs) with Fe(III) oxide coating and ethylene-diamine modification	On pH 4.0, an exchange between ions occurred, with an adsorption capacity of 23.47 mg/g.	[67]
MWCNT - zirconia nanohybrid (MWCNT-ZrO_2)	The initial concentration was 100mg/L. At pH 6.0 As^{+5} was removed with an adsorption capacity of 5000mg/g.	[68]
Iron oxide-coated MWCNT	The initial concentration was 100mg/L. At pH 4.0 As^{+5} was removed with an adsorption capacity of 189mg/g.	[69]
Graphene oxide carbon nanotube with αFeOOH coating	The adsorption capacity was 102.11 mg/g.	[70]

3.4.2. Lead (Pb) removal by using functionalized CNTs.

The surface area and configuration of CNTs are essential elements in heavy metal removal. CNTs' adsorption capacity rises when their external diameter is reduced, but CNTs' adsorption capacity enhances when their outer diameter is expanded by Sodium hypochlorite (NaClO). This demonstrates that the surface area and oxygen groups of multi-walled carbon (MWCNT) affect the adsorption process. Adsorption mechanisms comprising physisorption and chemisorption are highly efficient for removing lead [67].

The absorption of Pb^{2+} ions using CNTs in the adsorption process was also examined by Kabbashi *et al*. 2009, with special emphasis devoted to contact length, adsorbent dosage, pH, and agitation speed. The highest percentage of Pb^{2+} removed was 96.03 percent at 80 minutes, 40 mg/L at pH of 5, and 50 r/min swirling speed [68].

Aerogels comprised of graphene layers and carbon nanotubes (CNTs) were examined as a medium for removing lead by hydrothermal degradation of GO and CNTs in the presence of Fe^{2+} ions ($FeSO_4$ solution). Graphene CNT adsorption rate ranged from 230 to 415 mg/g.

The study showed that the quantities of $FeSO_4$ and CNT are two critical elements affecting removal effectiveness [69].

With an adsorption efficiency of 55.74 mg/g, zeolite carbon nanotubes (ZCNTs) were produced and used as a new technique for removing Pb^{2+} ions. The Langmuir isotherm model was fit to a pseudo-second-order by this ZCNTs kinetics model [70]. Furthermore, the reaction order of the absorbance was examined to study the hyperchromic impact on carboxylic CNTs for Pb^{2+} elimination [71]. Table 5 summarizes the functionalized carbon nanotubes (CNTs) utilized to remove lead and observations.

Table 5. Table Showing Functionalized CNTs used for Removal of Lead.

Adsorbent Applied	Observations/Comments	Reference
Acid-treated CS –CNTs	The affinity of adsorption was 158.7 mg/g.	[72]
CNTs with HNO_3 functionalization	The capacity of adsorption was 25.6 mg/g.	[73]
CNT complexes	The efficiency of this method was 99%.	[74]
Polyamine or CNT complexes	The capacity of adsorption was 3.2 mg/g.	[75]

3.4.3. Mercury (Hg) removal by using functionalized CNTs.

In research investigated by using CNTs surface modified with amino thiol for the adsorption of Hg^{2+}, the single-walled carbon nanotubes activated with thiol (SWCNTs-SH) attained adsorption effectiveness of 91 percent with a three times increment of adsorbed efficiency for Hg^{2+} ions in comparison to SWCNTs and a four times increment of adsorbed efficiency in comparison to activated carbon [72]. Another work combined magnetite nanocomposite/thiol-functionalized MWCNTs with mercaptopropyl triethoxysilane (MPTS) implanted onto the CNTs/Fe_3O_4 surfaces to create MPTS-CNTs/Fe_3O_4 nanocomposites for the eradication of both Pb^{2+} and Hg^{2+}. At a pH of 6.5, their adsorption capacities for Pb^{2+} and Hg^{2+} were 65.40 and 65.52 mg/g, respectively [73]. Because of the interaction between hydrogen (H^+) and metal ions and the inclination of metal ions to hydrate $M(OH)_2$ at higher pH levels, adsorption potential increased as pH increased, with 6.5 mg/g being the optimal pH for maximum adsorption.

The geometric dimensional impacts of non-oxidized and oxidized MWCNTs on Hg^{2+} absorption from water were studied. Likewise, MWCNTs functionalized with $KMnO_4/H_2SO_4$, and MWCNTs functionalized with HNO_3 have been described [74]. The pseudo-second-order best suited the experimental results, and the adsorption method was chemisorption according to the Elovich model.

The Langmuir equation also correctly described the isotherm models, with functionalized MWCNTs having a higher adsorption capacity than virgin MWCNTs. Lastly, MWCNTs containing sulfur (SMWCNTs) examined for Hg^{2+} reduction from the water were accomplished with a maximum sorption capacity of 72.8 mg/g [75]. Table 6 displays the many carbon nanotubes (CNTs) types that have been utilized to eliminate mercury and the influence of various factors on the metal ion adsorption process.

Table 6. Table showing functionalized CNT used for removal of mercury.

Adsorbent Applied	Observations/Comments	Reference
Carbon nanotubes with MnO_2 coating	The initial concentration was 10 mg/L, and after a contact time of 80 minutes at 50°C. The adsorption capacity was 58.82 mg/g.	[76]
COOH-MWCNTs	The initial concentration was 4 mg/L and with the help of Electrostatic Interaction at pH 4.3. The adsorption capacity was 127.6 mg/g.	[74]
WCNT with functionalized sulfur incorporation (CNT-S)	Removal of mercury occurs due to the process of ion exchange. With the initial concentration of 100-500 mg/L. At pH 6, removal occurred with an adsorption capacity of 151.51mg/g.	[77]
MWCNTs-Fe_3O_4	The adsorption capacity was found to be rather high, at 238.78 mg/g.	[78]

3.5. Removal of heavy metals using hydrogel.

A hydrogel is a three-dimensional (3D) lattice of hydrophilic polymers that establish their structure by physical and chemical bonding. The hydrogel's signature trait is its ability to expand in water and retain a high quantity of water while preserving its structure [76]. To be termed hydrogel, a substance must contain at least 10% of water by weight (or volume). In most circumstances, when the stimulus is withdrawn, the hydrogel returns to its original condition [77]. Some common types of hydrogels were examined, including pH, temperature, light, and electro-sensitive [78].

The solutions' pH greatly influences the hydrogel's capacity to adsorb metal ions. AM/AMPS (acrylamide/methylpropane sulfonic acid) hydrogels have significant adsorption capacity that elevates due to an increase in pH. Cd^{2+} (II) > Cu^{2+} > Fe^{3+} is the affinity order of metal ions in adsorption by hydrogel, which is thought to be influenced by polarization, electronic arrangement, ionic radius, and, most critically, the type of interaction with the hydrogel's functional groups [79].

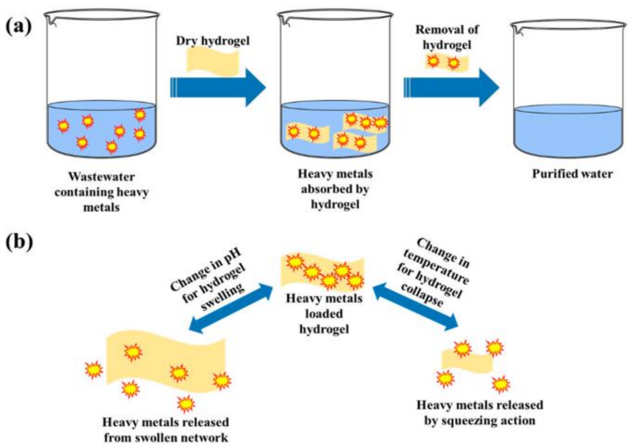

Figure 8. (**a**) Schematic description of the treatment of wastewater contaminated by heavy metals with the help of the hydrogel method; (**b**) Reversible reaction of change in structure due to stimuli (temperature and pH) [80].

Some studies discovered that under challenging circumstances, the binding capabilities of all metal ions decreased: 730–800 mg/g for Cd^{2+}, 650–720 mg/g for Cu^{2+}, and 610–700 mg/g for Fe^{3+}. Other metal ions' binding capabilities are 580–620, 610–680, 500–581, 300–350, and 200–280 mg/g for Zn^{2+}, Mn^{2+}, Co^{2+}, Pb^{+2}, and Na^{+}, respectively [81]. By reducing the pH of the solution, the absorbing metal ions within saturating AM/AMPS hydrogels could be desorbed. Cu^{2+}, Fe^{3+}, and Cd^{2+} recoveries were calculated to be 98.5%, 93%, and 94%, respectively, using AM (50 mol percent)/AMPS (50 mol percent) crossed linked with 10% N, N' -methylene bisacrylamide (MBA) [82].

Song *et al*. studied super adsorbents with extremely high adsorption capacities, which are very useful for successful wastewater cleanup. Super-adsorbent hydrogel spheres (SAHSs) are internally cross-linked polymers that act as self-sacrificing micro-reactors. They are synthesized by cross-linking polymerization of the hydrogel matrix followed by the time-controlled self-disintegration in less than 150 seconds. The hydrogel spheres of poly (2-acrylamido-2-methylpropanesulfonic acid-co-acrylic acid) displayed high adsorption capabilities for organic dyes and heavy metallic ions for Pb^{2+} [83].

Furthermore, the hydrogel demonstrated excellent recovery and recycling ability, selectivity sorption, and efficient separation-regeneration. Hydrogel particles made of chitosan and gelatin generated by inverse emulsion from chitosan, gelatin, and glutaraldehyde aqueous solutions had a maximum removal efficiency of 98% for Hg^{2+} ions in a solution [84].

The structure of the hydrogels, rather than the pore diameter or level of expansion, influenced the outcomes. In a multiple metal ion solution, removal effectiveness for Hg^{2+}, Pb^{2+}, Cr^{3+}, and Cd^{2+} ions was from 73% to 94% [85]. The results showed that the CG (chitosan-gelatin) hydrogel might be applied to recover co-existing heavy metal ions from wastewater, offering a flexible technique for removing various metal ions from natural or industrialized wastes [84].

3.6. Economic aspect and feasibility of adsorbents.

Adsorption is a more efficient and cost-effective metal removal method than other technologies used for wastewater treatment. This method produces effluent with noticeable high quality, giving it an advantage over the other methods. The ability to be regenerated and reused for several adsorption cycles makes this process the most feasible and economical method for heavy metal removal [86]. The expense of regeneration could be equivalent to or marginally higher than the cost of stabilization, but if the use of fresh adsorbent is minimized, several financial, commercial, and environmental advantages may be obtained especially in resource-limited countries. However, in these settings, the choice of techniques according to economic aspects is crucial.

Though carbon-derived adsorbents are the most popular for their efficiency, AC remains expensive to manufacture and difficult to dispose of with difficult and costly regeneration [87]. Therefore, non-conventional alternative adsorbents, such as agricultural waste, spent slurry, and industrial wastewater sludge, are preferred due to their wide availability, cost-effectiveness, and affinity for a wide variety of metal ions [88]. Agricultural wastes, such as rice husks, egg shells, wheat bran, coconut husks, palm fruit waste, walnut shell or groundnut shell, fruit peels waste, etc., have high adsorption capacity due to their composition of hydrocarbons (Table 7) [86]. These wastes are widely available, cheap, and can be modified into chars and later activated for reuse.

Table 7. Agricultural waste-based adsorbents used for heavy metal removal [86].

Wastewater type	Adsorbent type	Adsorbent dose (g/L)	Metal ion	Amount adsorbed	Contact time	Temperature (℃)	pH
Aqueous Solution	Ash Gourd Peel Powder	6.0	Cr^{6+}	18.70	40-60	28.0	1.0
Aqueous Solution	Barley Straw	1.0	Cu^{2+}	4.64	120	25.0	6.0-7.0
Aqueous Solution	Cashew Nut	3.0	Ni^{2+}	18.86	30	30.0	5.0

Wastewater type	Adsorbent type	Adsorbent dose (g/L)	Metal ion	Amount adsorbed	Contact time	Temperature (℃)	pH
Electroplating Wastewater	Chemically Modified Orange peel	2.0	Cu^{2+}	289.0	180	30.0	5.0
Aqueous Solution	Modified Lawny Grass	0.5	Pb^{2+}	137.12	400	29.85	6.0
Aqueous Solution	Grapefruit Peel	2.0	U^{6+}	140.79	60-80	24.85	4.0-6.0
Aqueous Solution	Peanut Shell	1.0	Cr^{6+}	4.32	360	30.0	2.0
Aqueous Solution	Sugar-cane, Orange Peel biochar	1.0	Pb^{2+}	86.96 and 27.86	30	25.0	5.0
Electroplating Wastewater	Mango Peel	5.0 5.0 5.0	Ni^{2+} Cu^{2+} Zn^{2+}	39.75 46.09 28.21	120	25.0	6.0
Aqueous Solution	Wheat Shell	10.0	Cu^{2+}	17.42	60	25.0	7.0
Aqueous Solution	Sulfonated Biochar	2.0	Pb^{2+} Cd^{2+}	191.07 85.76	5	180.0	4.5

Although testing has been performed on the adsorption of heavy metals of different adsorbent, research into regeneration remain limited. However, adsorbent recovery might be better than stabilizing adsorbents and restoring useful adsorbates, thereby decreasing demand for fresh adsorbent materials and further reducing costs. Biochar is another cheaper alternative obtained from the carbonization process of biomass [89,90]. They are solid with more carbon, hydrogen, and oxygen. They are more effective for removing heavy metals from wastewater than low-cost conventional and unconventional adsorbents due to their mesoporous structure with high surface area, different functional groups, and low ash [89,91].

4. Conclusions

Different adsorption techniques mentioned above could be utilized to remove heavy metals. The efficiency of the separation method depends on critical operational parameters such as pH, starting heavy metal concentration levels in wastewater, operating temperature, and others. In order to determine the properness of a certain method, many factors should be evaluated, such as the environmental effects, overall treatment effectiveness compared to other technology, as well as financial considerations such as capital expenditure and operating cost. Carbon NanoTubes (CNTs), Hydrogels, Graphene, Graphitic carbon nitride (g-C_3N_4), and Activated Carbon have great efficiency in removing heavy metals. Above mentioned techniques have proved to be highly efficient in dealing with heavy metals and some currently emerging issues like persistent and emerging organic pollutants. Due to their effectiveness, some rigorous research is being carried out to develop cost-efficient absorbents that will make these techniques favorable in economic respect.

5. Recommendations and Future Trends

The rising issues of water scarcity are leading the world towards rigorous research in the field of wastewater treatment as well as the treatment of contaminants from potable water. However, they have certain limits in regard to cost reliability and functionality of techniques such as Advanced Oxidation Processes (AOPs), Carbon Nanotubes (CNTs), Hydrogels, Graphene, Graphitic carbon nitride (g-C_3N_4), etc. An effective treatment method must have a high rejection level towards pollutants and be cost-efficient, making it a highly suitable product for its application on a commercial level. Choosing an adsorbent that meets both the efficiency requirements and cost-effectiveness can be a challenge. Additional studies should be conducted on introducing easy synthesis methods and cost-efficient raw materials to reduce costs and explore structural modifications and surface functionalization. Waste products' cost and ecological effect must be minimized before innovative materials can be used on a large scale in wastewater treatment. Cost-effective recycling procedures, sustainable disposal choices, and durability are also necessary for the practical deployment of new materials on a broad scale.

Funding

The authors declare that no funds, grants, or other support were received during the preparation of this manuscript.

Acknowledgments

The authors acknowledge support from Mohammed V University in Rabat and the Moroccan Ministry of Higher Education and Scientific Research for a Ph.D. fellowship to Abderrahim Maftouh (A.M.).

Conflicts of Interest

The authors declare no conflict of interest.

References

1. Darweesh, M.A.; Elgendy, M.Y.; Ayad, M.I.; Ahmed, A.M.M.; Elsayed, N.K.; Hammad, W. Adsorption isotherm, kinetic, and optimization studies for copper (II) removal from aqueous solutions by banana leaves and derived activated carbon. *South African Journal of Chemical Engineering* **2022**, *40*, 10-20, https://doi.org/10.1016/j.sajce.2022.01.002.
2. Fu, L.; Li, J.; Wang, G.; Luan, Y.; Dai, W. Adsorption behavior of organic pollutants on microplastics. *Ecotoxicology and Environmental Safety* **2021**, *217*, 112207, https://doi.org/10.1016/j.ecoenv.2021.112207.
3. Jaishankar, M.; Tseten, T.; Anbalagan, N.; Mathew, B.B.; Beeregowda, K.N. Toxicity, mechanism and health effects of some heavy metals. *Interdisciplinary toxicology* **2014**, *7*, 60, https://doi.org/10.2478/intox-2014-0009.
4. Tchounwou, P.B.; Yedjou, C.G.; Patlolla, A.K.; Sutton, D.J. Heavy metal toxicity and the environment. *Molecular, clinical and environmental toxicology* **2012**, *101*, 133-164, https://doi.org/10.1007/978-3-7643-8340-4_6.
5. Sankhla, M.S.; Kumar, R. Contaminant of heavy metals in groundwater & its toxic effects on human health & environment. *Available at SSRN 3490718* **2019**, https://doi.org/10.19080/IJESNR.2019.18.555996.
6. Fallah, Z.; Zare, E.N.; Khan, M.A.; Iftekhar, S.; Ghomi, M.; Sharifi, E.; Tajbakhsh, M.; Nikfarjam, N.; Makvandi, P.; Lichtfouse, Sillanpaa, M.; Varma, R.S. Ionic liquid-based antimicrobial materials for water treatment, air filtration, food packaging and anticorrosion coatings. *Advances in Colloid and Interface Science* **2021**, *294*, 102454, https://doi.org/10.1016/j.cis.2021.102454.
7. Barus, B.S.; Chen, K.; Cai, M.; Li, R.; Chen, H.; Li, C.; Wang, J.; Cheng, S.-Y. Heavy Metal Adsorption and Release on Polystyrene Particles at Various Salinities. *Frontiers in Marine Science* **2021**, *8*, 671802, https://doi.org/10.3389/fmars.2021.671802.
8. Wang, Q.; Zhu, S.; Xi, C.; Zhang, F. A Review: Adsorption and removal of heavy metals based on polyamide-amines composites. *Frontiers in Chemistry* **2022**, *10*, 814643, https://doi.org/10.3389/fchem.2022.814643.
9. Balali-Mood, M.; Naseri, K.; Tahergorabi, Z.; Khazdair, M.R.; Sadeghi, M. Toxic mechanisms of five heavy metals: mercury, lead, chromium, cadmium, and arsenic. *Frontiers in pharmacology* **2021**, *12*, 643972, https://doi.org/10.3389/fphar.2021.643972.
10. Giambò, F.; Italia, S.; Teodoro, M.; Briguglio, G.; Furnari, N.; Catanoso, R.; Costa, C.; Fenga, C. Influence of toxic metal exposure on the gut microbiota. *World Academy of Sciences Journal* **2021**, *3*, 1-1, https://doi.org/10.3892/wasj.2021.90.
11. Heng, Y.Y.; Asad, I.; Coleman, B.; Menard, L.; Benki-Nugent, S.; Hussein Were, F.; Karr, C.J.; McHenry, M.S. Heavy metals and neurodevelopment of children in low and middle-income countries: A systematic review. *PloS one* **2022**, *17*, e0265536, https://doi.org/10.1371/journal.pone.0265536.

12. Piñeiro, X.F.; Ave, M.T.; Mallah, N.; Caamaño-Isorna, F.; Jiménez, A.; Vieira, D.N.; Bianchini, F.; Muñoz-Barús, J.I. Heavy metal contamination in Peru: implications on children's health. *Scientific reports* **2021**, *11*, 1-9, https://doi.org/10.1038/s41598-021-02163-9.
13. Rajkumar, V.; Gupta, V. *Heavy metal toxicity*; In StatPearls. Treasure Island (FL): StatPearls Publishing: 2022. https://www.ncbi.nlm.nih.gov/books/NBK560920/
14. Alengebawy, A.; Abdelkhalek, S.T.; Qureshi, S.R.; Wang, M.-Q. Heavy metals and pesticides toxicity in agricultural soil and plants: Ecological risks and human health implications. *Toxics* **2021**, *9*, 42, https://doi.org/10.3390/toxics9030042.
15. Rajasekar, A.; Arunachalam, K.; Kottaisamy, M. Assessment of strength and durability characteristics of copper slag incorporated ultra high strength concrete. *Journal of Cleaner Production* **2019**, *208*, 402-414, https://doi.org/10.1016/j.jclepro.2018.10.118.
16. Santiago, A.R.; Medina, P.B.; Su, X. Electrochemical remediation of perfluoroalkyl substances from water. *Electrochimica Acta* **2022**, *403*, 139635, https://doi.org/10.1016/j.electacta.2021.139635.
17. Yadav, M.; Kumar, R.; Krishnamurthy, R. Chemistry of abiotic nucleotide synthesis. *Chemical reviews* **2020**, *120*, 4766-4805, https://doi.org/10.1021/acs.chemrev.9b00546.
18. Ali, I.; Mbianda, X.; Burakov, A.; Galunin, E.; Burakova, I.; Mkrtchyan, E.; Tkachev, A.; Grachev, V. Graphene based adsorbents for remediation of noxious pollutants from wastewater. *Environment international* **2019**, *127*, 160-180, https://doi.org/10.1016/j.envint.2019.03.029.
19. Maftouh, A.; El Fatni, O.; Fayiah, M.; Liew, R.K.; Lam, S.S.; Bahaj, T.; Butt, M.H. The application of water–energy nexus in the Middle East and North Africa (MENA) region: a structured review. *Applied Water Science* **2022**, *12*, 1-21, https://doi.org/10.1007/s13201-022-01613-7.
20. Fiyadh, S.S.; AlSaadi, M.A.; Jaafar, W.Z.; AlOmar, M.K.; Fayaed, S.S.; Mohd, N.S.; Hin, L.S.; El-Shafie, A. Review on heavy metal adsorption processes by carbon nanotubes. **2019**, *230*, 783-793, https://doi.org/10.1016/j.jclepro.2019.05.154.
21. Xie, R.-h.; Yuan, Y.-j.; Huang, J.-j. Different types of environmental regulations and heterogeneous influence on "green" productivity: evidence from China. *Ecological Economics* **2017**, *132*, 104-112, https://doi.org/10.1016/j.ecolecon.2016.10.019.
22. Saravanan, A.; Kumar, P.S.; Jeevanantham, S.; Karishma, S.; Tajsabreen, B.; Yaashikaa, P.; Reshma, B. Effective water/wastewater treatment methodologies for toxic pollutants removal: Processes and applications towards sustainable development. *Chemosphere* **2021**, *280*, 130595, https://doi.org/10.1016/j.chemosphere.2021.130595.
23. Zaimee, M.Z.A.; Sarjadi, M.S.; Rahman, M.L. Heavy metals removal from water by efficient adsorbents. *Water* **2021**, *13*, 2659, https://doi.org/10.3390/w13192659.
24. Pandey, L.M. Surface engineering of nano-sorbents for the removal of heavy metals: Interfacial aspects. *Journal of Environmental Chemical Engineering* **2021**, *9*, 104586, https://doi.org/10.1016/j.jece.2020.104586.
25. Ahmad, A.; Azam, T. Water purification technologies. In *Bottled and Packaged Water*; Elsevier: 2019; pp. 83-120, https://doi.org/10.1016/B978-0-12-815272-0.00004-0.
26. Karnib, M.; Kabbani, A.; Holail, H.; Olama, Z. Heavy metals removal using activated carbon, silica and silica activated carbon composite. *Energy Procedia* **2014**, *50*, 113-120, https://doi.org/10.1016/j.egypro.2014.06.014.
27. Hsu, S.-T.; Pan, T.-C. Adsorption of paraquat using methacrylic acid-modified rice husk. *Bioresource technology* **2007**, *98*, 3617-3621, https://doi.org/10.1016/j.biortech.2006.11.060.
28. Mohan, D.; Singh, K.P. Single-and multi-component adsorption of cadmium and zinc using activated carbon derived from bagasse—an agricultural waste. *Water research* **2002**, *36*, 2304-2318, https://doi.org/10.1016/S0043-1354(01)00447-X.
29. Hoang, A.T.; Kumar, S.; Lichtfouse, E.; Cheng, C.K.; Varma, R.S.; Senthilkumar, N.; Nguyen, P.Q.P.; Nguyen, X.P. Remediation of heavy metal polluted waters using activated carbon from lignocellulosic biomass: An update of recent trends. *Chemosphere* **2022**, 134825, https://doi.org/10.1016/j.chemosphere.2022.134825.
30. Dong, X.; Ma, L.Q.; Li, Y. Characteristics and mechanisms of hexavalent chromium removal by biochar from sugar beet tailing. *Journal of hazardous materials* **2011**, *190*, 909-915, https://doi.org/10.1016/j.jhazmat.2011.04.008.
31. Uchimiya, M.; Bannon, D.I.; Wartelle, L.H.; Lima, I.M.; Klasson, K.T. Lead retention by broiler litter biochars in small arms range soil: impact of pyrolysis temperature. *Journal of agricultural and food chemistry* **2012**, *60*, 5035-5044, https://doi.org/10.1021/jf300825n.
32. Wang, R.-s.; Li, Y.; Shuai, X.-x.; Liang, R.-h.; Chen, J.; Liu, C.-m. Pectin/activated carbon-based porous microsphere for Pb2+ adsorption: Characterization and adsorption behaviour. *Polymers* **2021**, *13*, 2453, https://doi.org/10.3390/polym13152453.
33. Low, S.S.; Pan, Y.; Ji, D.; Li, Y.; Lu, Y.; He, Y.; Chen, Q.; Liu, Q. Smartphone-based portable electrochemical biosensing system for detection of circulating microRNA-21 in saliva as a proof-of-concept. *Sensors and Actuators B: Chemical* **2020**, *308*, 127718, https://doi.org/10.1016/j.snb.2020.127718.

34. Maliyekkal, S.M.; Sreeprasad, T.; Krishnan, D.; Kouser, S.; Mishra, A.K.; Waghmare, U.V.; Pradeep, T. Graphene: a reusable substrate for unprecedented adsorption of pesticides. *small* **2013**, *9*, 273-283, https://doi.org/10.1002/smll.201201125.
35. Asif, M.B.; Iftekhar, S.; Maqbool, T.; Paramanik, B.K.; Tabraiz, S.; Sillanpää, M.; Zhang, Z. Two-dimensional nanoporous and lamellar membranes for water purification: reality or a myth?. *Chemical Engineering Journal* **2021**, 134335, https://doi.org/10.1016/j.cej.2021.134335.
36. Khraisheh, M.; Elhenawy, S.; AlMomani, F.; Al-Ghouti, M.; Hassan, M.K.; Hameed, B.H. Recent progress on nanomaterial-based membranes for water treatment. *Membranes* **2021**, *11*, 995, https://doi.org/10.3390/membranes11120995.
37. Ramesha, G.; Kumara, A.V.; Muralidhara, H.; Sampath, S. Graphene and graphene oxide as effective adsorbents toward anionic and cationic dyes. *Journal of colloid and interface science* **2011**, *361*, 270-277, https://doi.org/10.1016/j.jcis.2011.05.050.
38. Deng, D.; Pan, X.; Yu, L.; Cui, Y.; Jiang, Y.; Qi, J.; Li, W.-X.; Fu, Q.; Ma, X.; Xue, Q. Toward N-doped graphene via solvothermal synthesis. *Chemistry of Materials* **2011**, *23*, 1188-1193, https://doi.org/10.1021/cm102666r.
39. Shi, X.; Peng, X.; Zhu, J.; Lin, G.; Kuang, T. Synthesis of DOPO-HQ-functionalized graphene oxide as a novel and efficient flame retardant and its application on polylactic acid: Thermal property, flame retardancy, and mechanical performance. *Journal of colloid and interface science* **2018**, *524*, 267-278, https://doi.org/10.1016/j.jcis.2018.04.016.
40. Zhao, G.; Ren, X.; Gao, X.; Tan, X.; Li, J.; Chen, C.; Huang, Y.; Wang, X. Removal of Pb (II) ions from aqueous solutions on few-layered graphene oxide nanosheets. *Dalton transactions* **2011**, *40*, 10945-10952, https://doi.org/10.1039/c1dt11005e.
41. Basadi, N.; Ghanemi, K.; Nikpour, Y. l-Cystine-functionalized graphene oxide nanosheets for effective extraction and preconcentration of mercury ions from environmental waters. *Chemical Papers* **2021**, *75*, 1083-1093, https://doi.org/10.1007/s11696-020-01368-y.
42. Rao, Z.; Feng, K.; Tang, B.; Wu, P. Surface decoration of amino-functionalized metal–organic framework/graphene oxide composite onto polydopamine-coated membrane substrate for highly efficient heavy metal removal. *ACS Applied Materials & Interfaces* **2017**, *9*, 2594-2605, https://doi.org/10.1021/acsami.6b15873.
43. Zhang, P.; Gong, J.-L.; Zeng, G.-M.; Deng, C.-H.; Yang, H.-C.; Liu, H.-Y.; Huan, S.-Y. Cross-linking to prepare composite graphene oxide-framework membranes with high-flux for dyes and heavy metal ions removal. *Chemical Engineering Journal* **2017**, *322*, 657-666, https://doi.org/10.1016/j.cej.2017.04.068.
44. Liu, W.; Wang, D.; Soomro, R.A.; Fu, F.; Qiao, N.; Yu, Y.; Wang, R.; Xu, B. Ceramic supported attapulgite-graphene oxide composite membrane for efficient removal of heavy metal contamination. *Journal of Membrane Science* **2019**, *591*, 117323, https://doi.org/10.1016/j.memsci.2019.117323.
45. Shukla, A.K.; Alam, J.; Alhoshan, M.; Dass, L.A.; Ali, F.A.A.; Mishra, U.; Ansari, M.A. Removal of heavy metal ions using a carboxylated graphene oxide-incorporated polyphenylsulfone nanofiltration membrane. *Environmental Science: Water Research & Technology* **2018**, *4*, 438-448, https://doi.org/10.1039/C7EW00506G.
46. Zhang, Y.; Zhang, S.; Gao, J.; Chung, T.-S. Layer-by-layer construction of graphene oxide (GO) framework composite membranes for highly efficient heavy metal removal. *Journal of membrane science* **2016**, *515*, 230-237, https://doi.org/10.1016/j.memsci.2016.05.035.
47. Zhang, Y.; Zhang, S.; Chung, T.-S. Nanometric graphene oxide framework membranes with enhanced heavy metal removal via nanofiltration. *Environmental science & technology* **2015**, *49*, 10235-10242, https://doi.org/10.1021/acs.est.5b02086.
48. Abdi, G.; Alizadeh, A.; Zinadini, S.; Moradi, G. Removal of dye and heavy metal ion using a novel synthetic polyethersulfone nanofiltration membrane modified by magnetic graphene oxide/metformin hybrid. *Journal of membrane science* **2018**, *552*, 326-335, https://doi.org/10.1016/j.memsci.2018.02.018.
49. De Beni, E.; Giurlani, W.; Fabbri, L.; Emanuele, R.; Santini, S.; Sarti, C.; Martellini, T.; Piciollo, E.; Cincinelli, A.; Innocenti, M. Graphene-based nanomaterials in the electroplating industry: A suitable choice for heavy metal removal from wastewater. *Chemosphere* **2022**, *292*, 133448, https://doi.org/10.1016/j.chemosphere.2021.133448.
50. Chen, W.; Chen, S.; Liang, T.; Zhang, Q.; Fan, Z.; Yin, H.; Huang, K.-W.; Zhang, X.; Lai, Z.; Sheng, P. High-flux water desalination with interfacial salt sieving effect in nanoporous carbon composite membranes. *Nature nanotechnology* **2018**, *13*, 345-350, https://doi.org/10.1038/s41565-018-0067-5.
51. Xiao, H.; Zhu, J.; Thomas, A. Graphitic carbon nitride for photocatalytic degradation of sulfamethazine in aqueous solution under simulated sunlight irradiation. *Rsc Advances* **2015**, *5*, 105731-105734, https://doi.org/10.1039/C5RA21895K.
52. Idris, A.O.; Oseghe, E.O.; Msagati, T.A.; Kuvarega, A.T.; Feleni, U.; Mamba, B. Graphitic carbon nitride: a highly electroactive nanomaterial for environmental and clinical sensing. *Sensors* **2020**, *20*, 5743, https://doi.org/10.3390/s20205743.

53. Shen, C.; Chen, C.; Wen, T.; Zhao, Z.; Wang, X.; Xu, A. Superior adsorption capacity of g-C3N4 for heavy metal ions from aqueous solutions. *Journal of colloid and interface science* **2015**, *456*, 7-14, https://doi.org/10.1016/j.jcis.2015.06.004.
54. Akbari Dehkharghani, A. Comparative study on the removal of toxic metal ions by advanced carbon allotropes and g-C3N4 adsorbents: a case study from Sarcheshmeh copper mine. *Environmental Earth Sciences* **2019**, *78*, 1-10, https://doi.org/10.1007/s12665-019-8656-7.
55. Adewunmi, A.A.; Ismail, S.; Sultan, A.S. Carbon nanotubes (CNTs) nanocomposite hydrogels developed for various applications: a critical review. *Journal of Inorganic and Organometallic Polymers and Materials* **2016**, *26*, 717-737, https://doi.org/10.1007/s10904-016-0379-6.
56. Das, R.; Bandyopadhyay, R.; Pramanik, P. Carbon quantum dots from natural resource: A review. *Materials today chemistry* **2018**, *8*, 96-109, https://doi.org/10.1016/j.mtchem.2018.03.003.
57. Sarkar, B.; Mandal, S.; Tsang, Y.F.; Kumar, P.; Kim, K.-H.; Ok, Y.S. Designer carbon nanotubes for contaminant removal in water and wastewater: a critical review. *Science of the Total Environment* **2018**, *612*, 561-581, https://doi.org/10.1016/j.scitotenv.2017.08.132.
58. Saifuddin, N.; Raziah, A.; Junizah, A. Carbon nanotubes: a review on structure and their interaction with proteins. *Journal of Chemistry* **2013**, *2013*, https://doi.org/10.1155/2013/676815.
59. Fiyadh, S.S.; AlSaadi, M.A.; Jaafar, W.Z.; AlOmar, M.K.; Fayaed, S.S.; Mohd, N.S.; Hin, L.S.; El-Shafie, A. Review on heavy metal adsorption processes by carbon nanotubes. *Journal of Cleaner Production* **2019**, *230*, 783-793, https://doi.org/10.1016/j.jclepro.2019.05.154.
60. Frayyeh, W.M.; Mohammed, Z.B.; Mahmood, A.K. Removal of heavy metal ions from wastewater by carbon nanotubes (CNTs). *Engineering and Technology Journal* **2021**, *39*, 1939-1944, http://dx.doi.org/10.30684/etj.v39i12.789.
61. Hoang, A.T.; Nižetić, S.; Cheng, C.K.; Luque, R.; Thomas, S.; Banh, T.L.; Nguyen, X.P. Heavy metal removal by biomass-derived carbon nanotubes as a greener environmental remediation: A comprehensive review. *Chemosphere* **2022**, *287*, 131959, https://doi.org/10.1016/j.chemosphere.2021.131959.
62. Das, R.; Abd Hamid, S.B.; Ali, M.E.; Ismail, A.F.; Annuar, M.; Ramakrishna, S. Multifunctional carbon nanotubes in water treatment: the present, past and future. *Desalination* **2014**, *354*, 160-179, https://doi.org/10.1016/j.desal.2014.09.032.
63. Arora, B.; Attri, P. Carbon nanotubes (CNTs): a potential nanomaterial for water purification. *Journal of Composites Science* **2020**, *4*, 135, https://doi.org/10.3390/jcs4030135.
64. Gotovac, S.; Honda, H.; Hattori, Y.; Takahashi, K.; Kanoh, H.; Kaneko, K. Effect of nanoscale curvature of single-walled carbon nanotubes on adsorption of polycyclic aromatic hydrocarbons. *Nano Letters* **2007**, *7*, 583-587, https://doi.org/10.1021/nl0622597.
65. Zhang, S.; Shao, T.; Bekaroglu, S.S.K.; Karanfil, T. The impacts of aggregation and surface chemistry of carbon nanotubes on the adsorption of synthetic organic compounds. *Environmental science & technology* **2009**, *43*, 5719-5725, https://doi.org/10.1021/es900453e.
66. Andjelkovic, I.; Nesic, J.; Stankovic, D.; Manojlovic, D.; Pavlovic, M.; Jovalekic, C.; Roglic, G. Investigation of sorbents synthesised by mechanical–chemical reaction for sorption of As (III) and As (V) from aqueous medium. *Clean Technologies and Environmental Policy* **2014**, *16*, 395-403, https://doi.org/10.1007/s10098-013-0635-1.
67. Yu, F.; Wu, Y.; Ma, J.; Zhang, C. Adsorption of lead on multi-walled carbon nanotubes with different outer diameters and oxygen contents: kinetics, isotherms and thermodynamics. *Journal of Environmental Sciences* **2013**, *25*, 195-203, https://doi.org/10.1016/S1001-0742(12)60023-0.
68. Kabbashi, N.A.; Atieh, M.A.; Al-Mamun, A.; Mirghami, M.E.; Alam, M.; Yahya, N. Kinetic adsorption of application of carbon nanotubes for Pb (II) removal from aqueous solution. *Journal of Environmental Sciences* **2009**, *21*, 539-544, https://doi.org/10.1016/S1001-0742(08)62305-0.
69. Zhang, M.; Gao, B.; Cao, X.; Yang, L. Synthesis of a multifunctional graphene–carbon nanotube aerogel and its strong adsorption of lead from aqueous solution. *Rsc Advances* **2013**, *3*, 21099-21105, https://doi.org/10.1039/c3ra44340j.
70. Cherono, F.; Mburu, N.; Kakoi, B. Adsorption of lead, copper and zinc in a multi-metal aqueous solution by waste rubber tires for the design of single batch adsorber. *Heliyon* **2021**, *7*, e08254, https://doi.org/10.1016/j.heliyon.2021.e08254.
71. Venkata Ramana, D.; Kumar Reddy, D.H.; Kumar, B.N.; Seshaiah, K.; Chandra Rao, G.P.; Lu, C. Adsorption of Pb (II) from aqueous solutions by chemically modified zeolite supported carbon nanotubes: equilibrium, kinetic, and thermodynamic studies. *Separation Science and Technology* **2013**, *48*, 403-412, https://doi.org/10.1080/01496395.2012.690638.
72. Aslam, M.M.-A.; Kuo, H.-W.; Den, W.; Usman, M.; Sultan, M.; Ashraf, H. Functionalized carbon nanotubes (Cnts) for water and wastewater treatment: Preparation to application. *Sustainability* **2021**, *13*, 5717, https://doi.org/10.3390/su13105717.
73. Zhang, C.; Sui, J.; Li, J.; Tang, Y.; Cai, W. Efficient removal of heavy metal ions by thiol-functionalized superparamagnetic carbon nanotubes. *Chemical Engineering Journal* **2012**, *210*, 45-52, https://doi.org/10.1016/j.cej.2012.08.062.

74. Chen, P.H.; Hsu, C.-F.; Tsai, D.D.-W.; Lu, Y.-M.; Huang, W.-J. Adsorption of mercury from water by modified multi-walled carbon nanotubes: adsorption behaviour and interference resistance by co-existing anions. *Environmental technology* **2014**, *35*, 1935-1944, https://doi.org/10.1080/09593330.2014.886627.
75. Pillay, K.; Cukrowska, E.; Coville, N. Improved uptake of mercury by sulphur-containing carbon nanotubes. *Microchemical Journal* **2013**, *108*, 124-130, https://doi.org/10.1016/j.microc.2012.10.014.
76. Zhang, Y.; Zhao, M.; Cheng, Q.; Wang, C.; Li, H.; Han, X.; Fan, Z.; Su, G.; Pan, D.; Li, Z. Research progress of adsorption and removal of heavy metals by chitosan and its derivatives: A review. *Chemosphere* **2021**, *279*, 130927, https://doi.org/10.1016/j.chemosphere.2021.130927.
77. Bahram, M.; Mohseni, N.; Moghtader, M. An introduction to hydrogels and some recent applications. In *Emerging concepts in analysis and applications of hydrogels*; IntechOpen: 2016, http://dx.doi.org/10.5772/64301.
78. Joshi, M.K.; Lee, S.; Tiwari, A.P.; Maharjan, B.; Poudel, S.B.; Park, C.H.; Kim, C.S. Integrated design and fabrication strategies for biomechanically and biologically functional PLA/β-TCP nanofiber reinforced GelMA scaffold for tissue engineering applications. *International Journal of Biological Macromolecules* **2020**, *164*, 976-985, https://doi.org/10.1016/j.ijbiomac.2020.07.179.
79. Mubarak, S.A.; Ali, S.A.; Yaagoob, I.Y.; Mazumder, M.A. Design and Synthesis of a Dual-Purpose Superadsorbent Containing a High Density of Chelating Motifs for the Fast Mitigation of Methylene Blue and Pb (II). *ACS omega* **2020**, *5*, 27833-27845, https://doi.org/10.1021/acsomega.0c02860.
80. Darban, Z.; Shahabuddin, S.; Gaur, R.; Ahmad, I.; Sridewi, N. Hydrogel-Based Adsorbent Material for the Effective Removal of Heavy Metals from Wastewater: A Comprehensive Review. *Gels* **2022**, *8*, 263, https://doi.org/10.3390/gels8050263.
81. Atta, A.M.; Ismail, H.S.; Elsaaed, A.M. Application of anionic acrylamide-based hydrogels in the removal of heavy metals from waste water. *Journal of Applied Polymer Science* **2012**, *123*, 2500-2510, https://doi.org/10.1002/app.34798.
82. Gad, Y. Preparation and characterization of poly (2-acrylamido-2-methylpropane-sulfonic acid)/Chitosan hydrogel using gamma irradiation and its application in wastewater treatment. *Radiation Physics and Chemistry* **2008**, *77*, 1101-1107, https://doi.org/10.1016/j.radphyschem.2008.05.002.
83. Song, X.; An, J.; He, C.; Zhou, J.; Xu, Y.; Ji, H.; Yang, L.; Yin, J.; Zhao, W.; Zhao, C. A bioinspired strategy towards super-adsorbent hydrogel spheres via self-sacrificing micro-reactors for robust wastewater remediation. *Journal of Materials Chemistry A* **2019**, *7*, 21386-21403, https://doi.org/10.1039/C9TA05550A.
84. Perumal, S.; Atchudan, R.; Yoon, D.H.; Joo, J.; Cheong, I.W. Spherical chitosan/gelatin hydrogel particles for removal of multiple heavy metal ions from wastewater. *Industrial & Engineering Chemistry Research* **2019**, *58*, 9900-9907, https://doi.org/10.1021/acs.iecr.9b01298.
85. Bassam, R.; El Alouani, M.; Jabrane, M.; El Khattabi, E.H.; Tridane, M.; Belaaouad, S. Studies on the Removal of Cadmium Toxic Metal Ions by Natural Clays from Aqueous Solution by Adsorption Process. *Journal of Chemistry* **2021**, *2021*, https://doi.org/10.1155/2021/7873488.
86. Hussain, A.; Madan, S.; Madan, R. Removal of heavy metals from wastewater by adsorption. *Heavy Metals—Their Environmental Impacts and Mitigation* **2021**, https://doi.org/10.5772/intechopen.95841.
87. Bhatnagar, A.; Sillanpää, M.; Witek-Krowiak, A. Agricultural waste peels as versatile biomass for water purification–A review. *Chemical engineering journal* **2015**, *270*, 244-271, https://doi.org/10.1016/j.cej.2015.01.135.
88. Bhatnagar, A.; Sillanpää, M. Utilization of agro-industrial and municipal waste materials as potential adsorbents for water treatment—a review. *Chemical engineering journal* **2010**, *157*, 277-296, https://doi.org/10.1016/j.cej.2010.01.007.
89. Khalil, U.; Shakoor, M.B.; Ali, S.; Rizwan, M.; Alyemeni, M.N.; Wijaya, L. Adsorption-reduction performance of tea waste and rice husk biochars for Cr (VI) elimination from wastewater. *Journal of Saudi Chemical Society* **2020**, *24*, 799-810, https://doi.org/10.1016/j.jscs.2020.07.001.
90. Shen, Z.; Zhang, Y.; McMillan, O.; Jin, F.; Al-Tabbaa, A. Characteristics and mechanisms of nickel adsorption on biochars produced from wheat straw pellets and rice husk. *Environmental Science and Pollution Research* **2017**, *24*, 12809-12819, https://doi.org/10.1007/s11356-017-8847-2.
91. Ho, S.-H.; Yang, Z.-k.; Nagarajan, D.; Chang, J.-S.; Ren, N.-q. High-efficiency removal of lead from wastewater by biochar derived from anaerobic digestion sludge. *Bioresource technology* **2017**, *246*, 142-149, https://doi.org/10.1016/j.biortech.2017.08.025.