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Review

Enhanced Adsorption of Chromate and Arsenate Ions from Contaminated Water with Emphasis on Polyethylenimine Modified Materials: A Review

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Abstract: Heavy metals in water pose a great threat to human health, and water treatment remains a critical issue globally. Among various water treatment techniques, adsorption has been proven to be an excellent way to remove heavy metals from water due to its advantages, like low cost, availability, profitability, ease of operation, and efficiency. Heavy metals such as chromium and arsenic are present in water in the form of anions, while many common adsorbents, such as biochar and activated carbons, cellulose, chitosan, clays, and silica, tend to acquire a negative surface charge. The surface charge of the adsorbent plays a major role in its interaction with heavy metal ions. Polyethylenimine is a polymer with a high cationic charge density. Modification of these adsorbents with polyethylenimine results in higher selectivity for these anions. The adsorption capacity is related to the efficiency of the introduction of polyethylenimine, which depends on the surface properties of the adsorbent. This review focuses on the effect of modification with polyethylenimine on the adsorption capacity of common adsorbents for the removal of heavy metal ions, such as chromate and arsenate, from water.

Keywords: polyethylenimine; adsorption capacity; chromate; arsenate

Citation: Xanthopoulou, M.; Katsoyiannis, I.A. Enhanced Adsorption of Chromate and Arsenate Ions from Contaminated Water with Emphasis on Polyethylenimine Modified Materials: A Review. *Separations* **2023**, *10*, 441. https://doi.org/10.3390/separations10080441

Academic Editor: Dimosthenis Giokas

Received: 22 June 2023
Revised: 25 July 2023
Accepted: 5 August 2023
Published: 7 August 2023

1. Introduction

Heavy metals such as chromium and arsenic can be toxic to humans, even at low concentrations [1]. They can cause a range of health problems, such as damage to the nervous system, kidney damage, reproductive problems, and even cancer [1–3]. Heavy metals can also accumulate in the environment and cause damage to ecosystems [2]. They can enter the food chain and affect wildlife, including fish, birds, and mammals [1,3]. They can also contaminate soil and groundwater, which can have long-term effects on plants and animals [3]. Many countries have regulations on acceptable levels of heavy metals in drinking water and wastewater discharge. Failure to comply with these regulations can result in legal and financial penalties and damage to the reputation of companies and organizations [3]. Heavy metal contamination can have economic costs as well, such as the loss of productivity in agriculture, fisheries, and other industries. In addition, the costs of treating contaminated water and soil can be significant [3]. Therefore, removing heavy metals from water is crucial for protecting human health, preserving the environment, complying with regulations, and avoiding economic costs.

Hexavalent chromium is highly toxic and is classified as a human carcinogen by various health and environmental agencies, including the International Agency for Research on Cancer (IARC) and the United States Environmental Protection Agency (EPA) [4,5]. It poses severe health risks to humans, including an increased risk of lung cancer when inhaled. Chromium contamination of water, especially in the form of hexavalent chromium, is a global water-related problem due to various industrial activities, including electroplating, leather tanning, stainless steel production, and other metal processing operations [4].

Also, in locations with mafic or ultramafic volcanic or metamorphic rocks (rocks that are mostly composed of ferromagnesian minerals without quartz), high concentrations of chromium may naturally occur in groundwater [5]. These concentrations are common in serpentine-rich units and ophiolite complexes [5]. As a result, many communities and regions face exposure to elevated levels of hexavalent chromium, necessitating effective removal methods. Furthermore, chronic exposure to elevated levels of arsenic, particularly through contaminated drinking water, can lead to severe health problems, including skin lesions, peripheral neuropathy, cardiovascular diseases, and an increased risk of several types of cancer, such as skin, lung, bladder, and kidney cancer [4]. Arsenic contamination is a widespread issue, affecting millions of people worldwide. It is particularly prevalent in parts of South and Southeast Asia, including Bangladesh and India, where large populations are exposed to high levels of naturally occurring arsenic in groundwater [4]. An estimated 140 million people in at least 70 countries have been drinking water containing arsenic at levels above the WHO provisional guideline value of 10 μg/L [6]. This is consistent with recent statistical modeling, which suggests between 94 and 220 million people are at risk of exposure to elevated arsenic concentrations in groundwater [6]. This makes arsenic removal a significant concern in regions heavily reliant on groundwater for drinking and irrigation. Arsenic is naturally present in rocks and minerals, which can lead to its release into the environment through geological processes [4]. This natural occurrence, coupled with human activities such as mining and agricultural use of arsenic-containing pesticides, contributes to the global arsenic contamination problem [4]. Research on chromium and arsenic removal not only addresses environmental and health concerns but also fosters advancements in water treatment technologies. Studying efficient and cost-effective removal techniques benefits the overall field of water and wastewater treatment. These research efforts play a crucial role in safeguarding public health, preserving the environment, and ensuring access to safe drinking water for communities worldwide.

The predominant form of heavy metals in aquatic solutions depends on various factors such as pH, temperature, salinity, redox potential, and the presence of other chemical species. Generally, the most common form of heavy metals in aquatic solutions is dissolved species, which are in the form of ions [7]. Chromium can form chromate ($CrO_4{}^{2-}$) and dichromate ($Cr_2O_7{}^{2-}$) oxyanions in water [7]. Arsenic can form the arsenate ($AsO_4{}^{3-}$) and arsenite ($AsO_3{}^{3-}$) oxyanions in water [8].

There are several methods available for the remediation of heavy metals from water, and some of the most common ones are adsorption, precipitation, ion exchange, membrane filtration, and electrocoagulation [9]. Adsorption, which is a popular method for heavy metal removal from water, involves the use of adsorbent material to bind the heavy metal ions onto its surface, thereby removing the pollutant from the water [9]. Common adsorbents used for this purpose include activated carbon, clay, zeolites, and various modified materials [9]. Precipitation involves the addition of a chemical to the water to cause the heavy metal ions to form a solid precipitate, which can be removed from the water. Common precipitating agents include lime, sodium hydroxide, and sodium carbonate. Ion exchange involves the exchange of heavy metal ions in the water with other ions, such as sodium or hydrogen ions, which are attached to resin material. The heavy metal ions are adsorbed onto the resin, while the exchange ions are released into the water. Membrane filtration uses a membrane to separate the heavy metal ions from the water. The most commonly used membrane filtration methods for heavy metal removal are reverse osmosis and nanofiltration. Electrocoagulation involves the use of an electrical current to coagulate the heavy metal ions in the water, causing them to form a precipitate that can be removed by settling or filtration. However, it should be noted that each heavy metal removal technique has its own advantages and disadvantages, and the selection of the appropriate method depends on several factors such as the type and concentration of the heavy metal, the volume of water or wastewater to be treated, and the cost-effectiveness of the method [9].

Adsorption is often preferred over other techniques for heavy metal removal for several reasons [10]. It has high efficiency in removing heavy metals from water and wastewater, even at low concentrations. This is due to the large surface area of the adsorbent material, which can adsorb a significant amount of heavy metals per unit weight. It can be applied to several heavy metals, such as lead, cadmium, mercury, chromium, and arsenic, and is effective for both cationic and anionic forms of heavy metals. Adsorption is often a low-cost method compared to other heavy metal removal techniques because the adsorbent materials are often inexpensive, readily available, and can be regenerated and reused. It is also a simple process that requires minimal equipment and can be easily integrated into existing water and wastewater treatment systems. It also requires little maintenance and can operate under a wide range of conditions. Furthermore, it is an environmentally safe method for heavy metal removal because it does not produce any hazardous by-products or generate any secondary pollutants. The adsorbent materials used can also be disposed of safely or even recycled [10]. Overall, adsorption is a promising method for the removal of heavy metals from water and wastewater, and its effectiveness and efficiency make it an attractive option for industrial and environmental applications.

Adsorbents are materials that can adsorb both cationic and anionic species from a solution onto their surfaces. The adsorption process is based on the interactions between the adsorbent's surface and the ions or molecules in the surrounding medium [10]. The adsorption capacity and selectivity of an adsorbent depend on its surface properties, including the presence of specific functional groups. These functional groups can interact with different types of ions or molecules through various forces such as electrostatic interactions, hydrogen bonding, and van der Waals forces [10]. To target anions, adsorbents are typically modified to introduce specific functional groups that have an affinity for anionic species [11]. Polyethylenimine (PEI) is a versatile and suitable material for the modification of adsorbents due to several advantageous properties and characteristics [11]. PEI has a high density of amine groups (-NH_2), which can form coordination complexes with various metal ions and other contaminants. Additionally, it can be easily attached to the surface of different adsorbent materials, such as activated carbon, zeolites, or silica-based materials [11]. Moreover, PEI-modified adsorbents generally exhibit good chemical stability, which is essential for maintaining their adsorption capacity and structural integrity during extended usage [11]. Overall, the use of polyethylenimine as a modifier for adsorbents offers a promising and effective approach to enhance adsorption capabilities and address various environmental pollution challenges.

The objective of this review dealing with the modification of adsorbents with polyethylenimine is to provide a comprehensive and critical assessment of the application and effectiveness of PEI modification in enhancing adsorbents for pollutant removal and water treatment. This review aims to summarize existing literature and assess the impact of PEI modification on adsorption capacity and selectivity. It compares the performance of PEI-modified adsorbents with unmodified adsorbents and modification techniques. Also, it highlights their efficacy in removing chromate and arsenate ions from various water sources.

2. Adsorbents for Chromium and Arsenic Removal from Water

Common adsorbents such as biochar, activated carbon, cellulose, chitosan, clays, and silica-based adsorbents have distinct properties that enable them to effectively capture chromate and arsenate ions from aqueous solutions [12,13]. Adsorption occurs as metal ions are attracted and retained on the surface of the adsorbent material through various mechanisms, including electrostatic interactions, ion exchange, chelation, complexation, and surface adsorption. The high surface area, porosity, and functional groups present in these adsorbents enhance their adsorption capacity and selectivity for different heavy metal ions. The adsorption process is influenced by factors such as pH, temperature, contact time, concentration, and the presence of competing ions [14]. Understanding the adsorption behavior of common adsorbents is critical for designing effective water treatment technologies for heavy metal removal. Some common and effective water treatment technologies are ion exchange, adsorption, electrocoagulation, precipitation, and membrane filtration [9]. These decisions on the technologies to be used depend on the specific water quality requirements, the presence of contaminants or co-contaminants, and the intended water usage (e.g., drinking water, industrial processes, irrigation).

2.1. Biochar

Biochar, a carbonaceous material produced by the pyrolysis of organic waste, has gained increasing attention as an adsorbent for the removal of chromium and arsenic from contaminated water. The porous structure of biochar provides a high surface area and a unique surface chemistry that can interact with chromium and arsenic species, making it an effective adsorbent.

Numerous studies have described the employment of biochar for the removal of hexavalent chromium, Cr(VI), from water and wastewater. A study exploring the use of biochar produced from coconut shells as an adsorbent for the removal of Cr(VI) from aqueous solutions was conducted by Babel et al. (2004) [15]. The authors found that the biochar showed a maximum adsorption capacity of 4.72 mg/g for Cr(VI) at 25 mg/L. Moreover, the removal efficiency increased from 17% to 90% with the increase in dose from 0.5 to 6 g/L. They also found that the capacity of the biochar adsorption increased with ascending pH from 2 to 6 and then decreased at pH > 6.0. A further study examined the use of rice-straw biochar for Cr(VI) remediation from wastewater [16]. Zhou et al. (2019) found that the biochar resulting from rice straw revealed an adsorption capacity of 15 mg/g for Cr(VI) of 25–1000 mg/L. They also observed that the adsorption capacity of the biochar was maximum at pH 2 [16]. Ma et al. (2014) studied biochar derived from rice husk, and they found an adsorption capacity of 23.09 mg/g at pH 6.8 with the use of 1 g/L and initial Cr(VI) concentrations of 10–1000 mg/L [17]. Additionally, Chen et al. (2021) investigated the use of biochar derived from sugarcane bagasse as an adsorbent for the removal of Cr(VI) from contaminated water [18]. The authors found that the biochar exhibited an adsorption capacity of 7.14 mg/g. They also observed that the adsorption capacity of the biochar was not affected by factors such as pH and initial Cr(VI) concentration [18].

Concerning arsenic adsorption on biochar, a study investigated the use of biochar derived from rice husk for the removal of arsenic from contaminated water [19]. Samsuri et al. (2013) found that the biochar exhibited adsorption capacities for both As(III) and As(V) of 19.3 and 7.1 mg/g, respectively [19]. They observed that the adsorption capacity of the biochar increased with increasing pH up to 6 and then decreased for As(V). In contrast, it increased with increasing pH for As(III), with the maximum adsorption found at pH 8 and 9. Another study investigated the use of biochar derived from bamboo for the removal of arsenic from aqueous solutions [20]. Alchouron et al. (2020) found that the biochar exhibited a good adsorption capacity for As(V), with a maximum adsorption capacity of 49 mg/g at pH 7 and 25 °C [20]. They observed that the adsorption capacity increased with the increase in temperature.

These studies demonstrate that biochar can be an effective adsorbent for the removal of Cr(VI), As(III), and As(V) from aqueous solutions. However, further research is needed to optimize the synthesis and application of biochar as an adsorbent and to investigate its potential for real-world applications.

2.2. Activated Carbon

Activated carbon has been widely used as an adsorbent for the removal of various pollutants from aqueous solutions due to its high adsorption capacity, large surface area, and porous structure. Chromium is one of the contaminants that can be removed using activated carbon, and it is also a commonly used adsorbent for removing arsenic from water. The adsorption capacity of activated carbon is influenced by factors such as pH, contact time, concentration, and temperature [21].

Several studies have investigated the use of activated carbon for the removal of chromium from aqueous solutions. Pakade et al. (2017) examined Macadamia nutshell-derived activated carbon for Cr(VI) removal from aqueous solutions. They found a maximum adsorption capacity of 22.3 mg/g at pH 2 using 4 g/L of adsorbent and 100 mg/L of Cr(VI) initial concentration [22]. Valentín-Reyes et al. (2019) investigated the removal of Cr(VI) from aqueous solutions using activated carbon derived from wood [23]. The results showed a maximum adsorption capacity of about 45 mg/g at pH 6 using 2 g/L activated carbon for the initial concentrations of 10–500 mg/L Cr(VI). Another study by Tolkou et al. (2022) investigated coconut shell-derived activated carbon for the removal of Cr(VI). They found a maximum adsorption capacity of about 0.1 mg/g at pH 7 with the use of 0.5 g/L activated carbon and 100 µg/L Cr(VI) [21]. They observed that increasing the pH resulted in decreasing adsorption capacity, and the maximum capacity was found at pH 5.

The efficiency of activated carbon in arsenic removal from water has been demonstrated in various studies. For example, a study by Chuang et al. (2005) found that activated carbon derived from oat hulls removed arsenic from aqueous solutions at a range of 60% for the initial concentration of 25 µg/L [24]. The removal rate is further decreased with an increase in the initial concentration up to 200 µg/L, while the maximum adsorption capacity is 3.09 mg/g at pH 5. Similarly, a study by Nieto-Delgado et al. (2019) reported that bituminous-based activated carbon exhibited a maximum adsorption capacity of about 2 mg/g for As(V) at pH 7 for initial concentrations up to 6 mg/L with the use of 0.8 g/L of activated carbon [25]. Another study by Kalaruban et al. (2019) investigated the use of commercial granular activated carbon for arsenic removal [26]. They found a maximum adsorption capacity of 1 mg/g with the use of 0.1 mg/L at pH 6 for initial concentrations up to 100 µg/L.

In conclusion, activated carbon is a promising adsorbent for chromium and arsenic removal from water. Its high surface area and porosity make it an effective adsorbent, although it may have some limitations. Further research is needed to optimize the use of activated carbon and explore the potential of modifying activated carbon to enhance its adsorption capacity and selectivity.

2.3. Cellulose

Cellulose, a biopolymer consisting of glucose units, has been extensively investigated as an adsorbent for the removal of heavy metals from aqueous solutions, including chromium and arsenic. Cellulose-based adsorbents have a high surface area and excellent chemical stability, making them promising candidates for heavy metal remediation. The adsorption mechanisms involve the formation of hydrogen bonds, electrostatic interactions, and ligand exchange between the heavy metal ion species and the cellulose surface [27].

Several studies have reported the effectiveness of cellulose-based adsorbents for the removal of chromium ions from aqueous solutions. Anirudhan et al. (2009) investigated commercial cellulose for the removal of Cr(VI), which exhibited a maximum adsorption capacity of 12.5 mg/g at pH 3.5 with the use of 2 g/L cellulose and an initial Cr(VI) concentration of 50 mg/L [27]. Similarly, Yang et al. (2014) investigated cellulose nanofibers as an adsorbent for Cr(VI), which showed a maximum adsorption capacity of about 30 mg/g at pH 4 for the initial concentration of 50 mg/L Cr(VI) [28]. In another study, Awang et al. (2018) developed a cellulose membrane for the removal of Cr(VI) from aqueous solutions. The cellulose membrane exhibited a maximum adsorption capacity for Cr(VI) ions of about 13 mg/g at pH 2 with the use of 1 g/L adsorbent and a 100 mg/L initial Cr(VI) concentration [29]. Another study by Pattarith et al. (2023) that studied cellulose for chromium adsorption from aqueous solutions found that cellulose material exhibited a maximum adsorption capacity of 23.5 mg/g for an initial chromium concentration of 100 mg/L and a dose of 0.2 g/L of the adsorbent at 30 °C and pH 3 [30].

Deng et al. (2016) reported the use of cellulose fibers for the removal of arsenic from aqueous solutions [31]. The adsorbent showed an adsorption capacity < 5 mg/g with the use of 0.4 g/L for the initial As(V) concentration of 150 mg/L at pH 1–10. Another study by Chai et al. (2022) investigated cellulose nanocrystals [32]. The adsorbent showed a maximum arsenic adsorption capacity of about 10 mg/g at pH 3 with the use of 0.1 g/L of adsorbent.

Overall, cellulose-based adsorbents have shown great potential for the removal of chromium and arsenic ions from aqueous solutions. Further research is needed to optimize the synthesis and functionalization of cellulose-based adsorbents for enhanced adsorption capacity and selectivity.

2.4. Chitosan

Chitosan is a biopolymer derived from chitin, which is a natural polymer found in the exoskeleton of crustaceans and insects. Chitosan has been extensively studied as an adsorbent for various heavy metals, including chromium and arsenic. The amino and hydroxyl groups on the chitosan surface enable it to form strong coordination complexes with arsenic species, leading to efficient removal from water [33]. Several studies have reported varying adsorption capacities for chitosan towards chromium and arsenic, and the efficiency can be further improved through modification with polyethylenimine or other functional groups.

Wan Ngah et al. (2006) studied the adsorption capacity of chitosan beads for Cr(VI) [33]. They found a maximum adsorption capacity of 76.92 mg/g at pH 3, using 0.1 g/L chitosan beads and 4–14 mg/L initial Cr(VI) concentration. Also, Baroni et al. (2008) found that chitosan exhibited an adsorption capacity of 65 mg/g at pH 6 with the use of 6 g/L and an initial Cr(VI) concentration of 250 mg/L [34]. Another study by Vakili et al. (2018) reported an adsorption capacity of 23.4 mg/g for chitosan hydrogel beads oriented towards chromium using 0.2 g/L of chitosan and a 20 mg/L initial Cr(VI) concentration [35]. The maximum adsorption capacity was achieved at pH 4, while it decreased at pH 2 and over 4.

Concerning arsenic adsorption, Kwok et al. (2014) investigated chitosan for the removal of arsenate ions. They found a maximum adsorption capacity of 1.2 mg/g using 0.5 g/L chitosan and initial arsenate concentrations of 1–10 mg/L at a pH range of 3.5–5.5 [36]. The maximum adsorption capacity was found at pH 3.5 and decreased at higher pH values. Another study by Kloster et al. (2020) also investigated the use of chitosan as an adsorbent for arsenic removal. They found a maximum adsorption capacity of 33.87 mg/g for arsenate ions using 10 g/L of adsorbent and 5–500 mg/L initial As(V) concentrations at pH 3 [37].

Overall, chitosan has shown great potential as an effective adsorbent for the removal of chromium and arsenic from aqueous solutions. However, the practical application of chitosan-based adsorbents for large-scale chromium and arsenic removal still faces challenges. Further research is needed to optimize the adsorbent preparation, improve its reusability, and develop cost-effective approaches.

2.5. Clays

Clays are abundant and inexpensive natural minerals that have been widely studied as potential adsorbents for the removal of various pollutants, including chromium and arsenic. Clays have been demonstrated to be efficient at removing heavy metals from contaminated water due to their large surface area, porosity, and high adsorption capability. The adsorption mechanism is mainly ascribed to electrostatic attraction, ion exchange, and surface complexation [38].

One of the commonly studied clays for chromium removal is bentonite. Bentonite is a naturally occurring clay mineral composed mainly of montmorillonite, which has a high cation exchange capacity and can be easily modified with various chemicals. Barkat et al. (2014) studied the removal efficiency of bentonite clay for hexavalent chromium [38]. Bentonite showed a maximum adsorption capacity of 12.61 mg/g with the use of 25 g/L at pH 5 for initial Cr(VI) concentrations of 50–200 mg/L, and the adsorption capacity decreased at lower pH values. Foroutan et al. (2018) also investigated bentonite for Cr(VI) removal, which exhibited a maximum adsorption capacity of 59.5 mg/g with the use of 1 g/L and 10–100 mg/L initial Cr(VI) concentrations at pH 3 [39]. Fayazi et al. (2020) investigated magnetic montmorillonite clay as an adsorbent for Cr(VI). They found a maximum adsorption capacity of about 35 mg/g using 3 g/L of the adsorbent and a 350 mg/L initial chromium concentration at pH 2 [40].

Kaolin is another type of clay that has been investigated for chromium removal. Kaolin is a layered silicate mineral with a high surface area and porosity, which makes it a promising adsorbent. Ajouyed et al. (2011) investigated kaolin as an adsorbent for Cr(VI) removal. Kaolin exhibited a maximum adsorption capacity of 0.57 mg/g at pH 8 with the use of 4 g/L of adsorbent and initial Cr(VI) concentrations of 0.1–16 mg/L [41]. Other clays that have been studied for chromium removal include illite and halloysite. Illite is a layered silicate mineral and showed a maximum adsorption capacity of 0.27 mg/g for chromium in a study by Ajouyed et al. (2011) [41]. They used for the adsorption study 4 g/L of adsorbent and initial Cr(VI) concentrations of 0.1–16 mg/L. Halloysite is a clay mineral that has a unique tubular structure. The tubular structure of the halloysite provides an ideal environment for adsorption, allowing for high sorption capacities and efficient removal of contaminants from aqueous solutions. Tian et al. (2015) investigated halloysite nanotubes as an adsorbent for chromium [42]. They found that halloysite nanotubes exhibited a maximum adsorption capacity of 1.3 mg/g at pH 2 with the use of 1.1 g/L of adsorbent and initial Cr(VI) concentrations of 30–260 mg/L.

The most commonly studied clays for arsenic removal are montmorillonite, kaolin, and illite. Mohapatra et al. (2007) examined montmorillonite, kaolin, and illite for As(V) removal from water. They found that the adsorption capacity was 0.64, 0.86, and 0.52 mg/g at pH 5 for montmorillonite, kaolin, and illite, respectively [43]. They used 40 g/L of each adsorbent and 10–200 mg/L As(V) initial concentrations. They found that As(V) adsorption for all three clay adsorbents is nearly consistent in the lower acidic pH range of 2.0 to 5.0 and then reduces when pH is increased further. Another study by Ren et al. (2014) found that montmorillonite exhibited a maximum adsorption capacity of about 0.5 mg/g with the use of a 4 g/L adsorbent and a 5 mg/L As(V) initial concentration [44].

Overall, clays have shown potential as low-cost adsorbents for the removal of chromium and arsenic from contaminated water. However, further studies are needed to optimize their adsorption performance and evaluate their feasibility for large-scale applications.

2.6. Silica

Silica is a naturally occurring mineral that has been widely used as an adsorbent for the removal of various contaminants from water, including chromium and arsenic. Non-modified silica has been shown to have a relatively low adsorption capacity for chromium. The adsorption mechanism of chromium on silica is primarily through electrostatic attraction and surface complexation. A study conducted by Jang et al. (2020) found that amorphous silica nanoparticles and mesoporous silica nanoparticles had a maximum adsorption capacity for chromium of 0.4 and 1.3 mg/g, respectively, at pH 2 using 2 g/L of adsorbent and 100 mg/L Cr(VI) initial concentration [45]. Similarly, another study by Najafi et al. (2021) reported that silica had an adsorption capacity of 4.6 mg/g for chromium at pH 3 with the use of a 3 g/L adsorbent and a Cr(VI) initial concentration of 50 mg/L [46].

In its natural form, silica has a limited affinity for arsenic due to a lack of functional groups [47]. However, some studies have demonstrated that non-modified silica can still adsorb arsenic from water. The adsorption mechanism is believed to involve electrostatic attraction and surface complexation between arsenic species and silanol groups on the silica surface. One study found that a silica-based material could effectively adsorb arsenic, with an adsorption capacity of 0.224 mg/g using 20 g/L and 0.03–20 mg/L As(V) initial concentrations [48]. In this study, Oyediji Aremu et al. (2019) found that the maximum adsorption capacity was at pH 8.5 and decreased at lower pH values. Another study by Numpilai et al. (2022) reported that porous silica could adsorb up to 0.5 mg/g of arsenic from an aqueous solution at pH 5, with an initial As(V) concentration of 5 mg/L and an adsorbent dosage of 1 g/L [49].

Overall, non-modified silica has shown great potential as an adsorbent for chromium and arsenic removal from water. However, further research is needed to optimize the adsorption process and evaluate the feasibility of using silica on a larger scale.

2.7. Discussion

It is essential to propose a unified Cr(VI) and As(V) removal mechanism in light of the previously mentioned various types of materials and their performances. This will help in unraveling the differences in the comparative performances of the various materials that have been synthesized and tested. The adsorption mechanisms of chromate and arsenate ions onto various adsorbents involve a combination of physical and chemical processes. Chromate and arsenate ions are anionic species, while many adsorbents possess negative or positive charged functional groups on surfaces under certain conditions [10]. The electrostatic interaction between the positively charged surface and the negatively charged ions makes adsorption possible. Functional groups such as hydroxyl (-OH), carboxyl (-COOH), amino (-NH_2), and silanol (-Si-OH) groups can interact with the ions through electrostatic interactions, ligand exchange, or coordination bonds [43–48]. Chitosan, for example, possesses positively charged amino groups that can attract and retain chromate and arsenate ions through electrostatic interactions [46]. Surface complexation plays a crucial role in the adsorption of both chromate and arsenate ions.

As it is shown in Table 1, the adsorption is favorable mostly at acidic and at least circumneutral pH conditions for chromate and arsenate ions, respectively, which is relevant to the surface charge depending on the functional groups of each adsorbent. Concerning Cr(VI), chitosan beads, commercial raw chitosan, commercial bentonite, chitosan commercial hydrogel beads, biochar from rice husk, and Macadamia nutshell activated carbon are the most effective on Cr(VI) removal. Concerning As(V), the most effective adsorbents are commercial chitosan, biochar from bamboo, and cellulose nanocrystals. The fact that chitosan adsorbents are the most effective for both chromate and arsenate ions is due to their positive surface charge related to their amino group content. Regarding the adsorbent materials that are more effective than other same-based materials, it seems that it depends on the raw material that they are derived from.

Table 1. Adsorption capacity for Cr(VI) and As(V) of various adsorbents.

Adsorbent	Adsorbent Dose (g/L)	Adsorption Capacity (mg/g)	pH	Initial Concentration (mg/L)	Ref
Biochar from coconut shells	6	4.72 Cr(VI)	6	25	[15]
Biochar from rice straw	2	15 Cr(VI)	2	25–1000	[16]
Biochar from rice husk	1	23.09 Cr(VI)	6.8	10–1000	[17]
Biochar from sugarcane bagasse	1	7.14 Cr(VI)	2	25–100	[18]
Macadamia nutshell-activated carbon	4	22.3 Cr(VI)	2	100	[22]
Activated carbon from wood	2	45 Cr(VI)	6	10–500	[23]
Coconut shell-activated carbon	0.5	0.1 Cr(VI)	7	100	[21]
Commercial cellulose	2	12.5 Cr(VI)	3.5	50	[27]
Cellulose nanofibers	2	30 Cr(VI)	4	50	[28]
Cellulose membrane	1	13 Cr(VI)	2	100	[29]
Cellulose material	0.2	23.5 Cr(VI)	3	100	[30]
Chitosan beads	0.1	76.92 Cr(VI)	3	4–14	[33]
Commercial raw chitosan	6	65 Cr(VI)	6	250	[34]
Chitosan hydrogel beads	0.2	23.4 Cr(VI)	4	20	[35]
Bentonite clay	25	12.61 Cr(VI)	5	50–200	[38]
Commercial bentonite	1	59.5 Cr(VI)	3	10–100	[39]
Kaolin	4	0.57 Cr(VI)	8	0.1–16	[41]
Illite	4	0.27 Cr(VI)	8	0.1–16	[41]
Halloysite	1.1	1.3 Cr(VI)	2	30–260	[42]
Magnetic Montmorillonite clay	3	35 Cr(VI)	2	350	[40]

Table 1. *Cont.*

Adsorbent	Adsorbent Dose (g/L)	Adsorption Capacity (mg/g)	pH	Initial Concentration (mg/L)	Ref
Amorphous silica nanoparticles	2	0.4 Cr(VI)	2	100	[45]
Mesoporous silica nanoparticles	2	1.3 Cr(VI)	2	100	[45]
Silica	3	4.6 Cr(VI)	3	50	[46]
Biochar from rice husk	5	7.1 As(V)	8–96	3–300	[19]
Biochar from bamboo	10	49 As(V)	7	0.16	[20]
Activated carbon from oat hulls	0.015	3.09 As(V)	5	0.025–0.2	[24]
Bituminous-based activated carbon	0.8	2 As(V)	7	6	[25]
Commercial activated carbon	0.1	1 As(V)	6	0.1	[26]
Cellulose fibers	0.4	5 As(V)	1–10	150	[31]
Cellulose nanocrystals	0.1	10 As(V)	3	5–500	[32]
Commercial chitosan flakes	0.5	1.2 As(V)	3.5	1–10	[36]
Commercial chitosan	10	33.87 As(V)	3	5–500	[37]
Montmorillonite	40	0.64 As(V)	5	10–200	[43]
Kaolin	40	0.86 As(V)	5	10–200	[43]
Illite	40	0.52 As(V)	5	10–200	[43]
Commercial montmorillonite	4	0.5 As(V)	4	5	[44]
Silica	20	0.224 As(V)	8.5	0.03–20	[48]
Porous silica	1	0.5 As(V)	5	5	[49]

3. Polyethylenimine Modification of Adsorbents

Polyethylenimine modification refers to the process of chemically grafting or attaching PEI molecules onto the surface of various materials or adsorbents to enhance their properties for specific applications, particularly in water treatment and environmental remediation [11]. PEI is a cationic polymer with a high density of amine groups (-NH_2), which gives it unique characteristics that make it a valuable modifier for sorbents and other materials [11]. The modification of materials with PEI involves several steps. Initially, the material's surface is activated to create reactive sites, which can then react with PEI molecules through covalent bonding or other interactions. The modification can be achieved through physical adsorption, electrostatic interactions, or chemical cross-linking, depending on the material and application [11]. The amine groups in PEI serve as functional sites for chemical interactions, increasing the number of adsorption sites on the modified material. This modification significantly enhances the material's adsorption capacity for various pollutants, such as heavy metals. Also, PEI modification allows for selective adsorption of specific contaminants due to the chemical affinity between the amine groups in PEI and certain pollutants [11]. This selectivity is beneficial when targeting specific contaminants in complex mixtures. PEI-modified materials can exhibit pH-dependent adsorption behavior, meaning their adsorption capacity can vary with changes in the solution's pH [11]. This property allows for fine-tuning the adsorption process based on environmental conditions. Some PEI-modified materials can be regenerated and reused after reaching their adsorption capacity. This regenerability makes them cost-effective and environmentally friendly, reducing waste generation. The covalent or electrostatic bonding of PEI onto the material's surface enhances its stability, reducing the risk of PEI leaching and improving long-term performance. PEI modification can be applied to a wide range of materials, including activated carbon, zeolites, silica-based materials, and other porous substrates, offering versatility for tailored solutions [11]. The modification of materials with PEI continues to drive research advancements in water treatment and environmental technologies, leading to the development of innovative and efficient pollutant removal methods. Overall, PEI modification is a valuable technique that enhances the performance of materials for pollutant removal and water treatment applications, contributing to cleaner water resources and environmental protection.

3.1. Surface Properties and Chemical Functionality of Adsorbents

The behavior and effectiveness of the adsorbent in adsorption applications are greatly influenced by the surface features, such as functional groups and surface charge. Biochar surfaces can possess various functional groups, such as hydroxyl (-OH), carboxyl (-COOH), and phenolic (-Ph) groups. These functional groups can contribute to the biochar's chemical reactivity, interactions with contaminants, and behavior in aquatic environments. The surface of biochar can carry a net positive or negative charge depending on the pH of the solution added and the presence of functional groups. Surface charge influences the biochar's interactions with ions, such as adsorption or desorption, as well as the attraction or repulsion of charged contaminants [50].

Activated carbon surfaces can contain a variety of surface functional groups, which contribute to their adsorption properties. The specific functional groups present can depend on the precursor material used for activation and the activation process itself. Some common surface functional groups found on activated carbon are carbonyl groups (C=O), which can contribute to the activated carbon's adsorption capacity for certain organic compounds; carboxyl groups (-COOH), which enhance the activated carbon's adsorption of polar compounds; hydroxyl groups (-OH), which can participate in hydrogen bonding interactions with polar molecules; and ether groups (-O-), which can also contribute to the activated carbon's reactivity and interactions with certain compounds. The surface charge of activated carbon is typically pH-dependent and arises from the presence of functional groups. At a specific pH, the activated carbon surface can be positively charged (cationic), negatively charged (anionic), or electrically neutral [51].

Cellulose is composed of glucose units, and the surface of cellulose fibers can contain various functional groups that contribute to its properties. Some surface functional groups are hydroxyl groups (-OH), which contribute to its highly hydrophilic character and to interaction with other polar substances through hydrogen bonding; acetyl groups (-$COCH_3$), which can influence the solubility; carboxyl groups (-COOH), which contribute to the surface charge of cellulose; and ether linkages (C-O-C), which contribute to the overall stability and strength of cellulose fibers. The surface charge of cellulose depends on the pH of the surrounding environment and the presence of functional groups [52].

The main surface functional groups of chitosan are amino groups (-NH_2), which are responsible for chitosan's cationic nature and its ability to be protonated or deprotonated depending on the pH of the environment. Their presence allows chitosan to form complexes with negatively charged molecules through electrostatic interactions; hydroxyl groups (-OH), which contribute to hydrophilicity and its ability to form hydrogen bonds with polar substances; and acetyl groups (-$COCH_3$) that can be partially or completely removed through deacetylation, resulting in varying degrees of deacetylation that affect the surface charge and properties of chitosan. The presence of amino groups on the surface of chitosan allows it to exhibit cationic behavior, especially under acidic conditions. The cationic nature of chitosan enables it to interact with negatively charged molecules, such as pollutants, through electrostatic interactions [53].

Clays are naturally occurring minerals belonging to the phyllosilicate group that have a layered structure composed of stacked silicate sheets. The surface of clays is rich in various functional groups, which contribute to their unique properties. The main surface functional groups are silanol groups (-Si-OH), which contribute to the hydrophilicity of clays and allow for interactions with polar substances. They can also be involved in chemical reactions and ion exchange processes; alumina groups (-Al-OH) in some clays, such as kaolinite and halloysite, can participate in various chemical reactions, including acid-base reactions and coordination with other ions or molecules. Isomorphic substitutions occur when the substitution of one element for another occurs within the crystal lattice. This substitution can lead to the presence of different functional groups on the clay surface, such as hydroxyl groups (-OH) or carboxyl groups (-COOH). Moreover, clays possess exchangeable cations such as sodium (Na^+), calcium (Ca^{2+}), or potassium (K^+), which reside in the interlayer spaces between clay layers. These cations can be exchanged with other cations in solution through ion exchange processes, allowing clays to act as ion exchangers. Clays have a net negative charge due to isomorphic substitutions within the crystal lattice. This negative charge is balanced by exchangeable cations, and it can vary depending on the pH and the nature of the solution environment [54].

Silica is a naturally occurring compound that can exist in various forms, including amorphous silica and crystalline forms such as quartz, cristobalite, and tridymite. The main surface functional groups of silica are silanol groups (-Si-OH), which are the predominant functional groups of silica. They contribute to its hydrophilic nature and can interact with water and other polar substances. Siloxane bonds (-Si-O-Si-) contribute to the overall stability and structure of silica materials and surface silanol species, depending on their acidity or basicity. Acidic silanol groups (-Si-OH) have a dissociated proton, making them negatively charged (anionic) under neutral or basic conditions. Basic silanol groups (+Si-OH_2) have an additional proton, making them positively charged (cationic) under acidic conditions. Under neutral pH, silica surfaces typically carry a net negative charge due to the dissociation of silanol groups. The charge density can vary depending on factors such as the density of silanol groups, the surface area, and the degree of hydration [55].

At neutral pH, the oxygenated functional groups of adsorbents, such as silica or activated carbon, tend to be negatively charged (anionic) [56]. As mentioned previously, chromate and arsenate ions are negatively charged, and the adsorbents mentioned above have plenty of oxygenated groups. Consequently, there is little or no electrostatic interaction between these adsorbents and chromate and arsenate anions. Surface modification of adsorbents such as biochar and activated carbon, cellulose and chitosan, clays, and silica with polyethylenimine (PEI) is a process that involves coating the surface of the adsorbent particles with the polymer PEI. This modification can enhance the properties and functionalities of biochar for various applications.

Polyethylenimine (PEI) is a polymer made up of repeating units of the compound ethylenimine. It is a highly branched and cationic polymer, meaning that it carries a positive charge along its molecular structure. PEI has a variety of applications due to its unique properties, including its ability to form complexes with negatively charged compounds. This property has made it useful as a coating for surfaces to improve adhesion [57]. PEI has a large number of amine groups that can bind strongly with chromate and arsenate ions. Another advantage of using PEI-based adsorbent materials is their ease of synthesis. PEI can be easily modified to form different types of adsorbent materials with varying properties. For example, PEI can be cross-linked with other polymers or impregnated onto porous materials such as silica gel and activated carbon.

3.2. PEI-Modified Adsorbents for Chromium Removal

The addition of PEI to biochar can enhance its adsorption capacity for Cr(VI) due to the amine groups present in the PEI, which can form a complexation with the Cr(VI) ions. Ma et al. (2014) synthesized and investigated the use of PEI-modified biochar derived from rice husk by fast pyrolysis at 723–773 K for the removal of Cr(VI) from aqueous solutions. They prepared PEI–biochar by treating the pristine biochar with HNO_3 or KOH solutions. The modification process took place by mixing the acid- or alkali-treated biochar with PEI/methanol solutions at a concentration of 10%. The authors found that the PEI-modified acid-biochar and PEI-modified alkali–biochar exhibited a maximum adsorption capacity for Cr(VI) of 60.78 mg/g and 435.7 mg/g, respectively, at pH 6.8 with the use of 1 g/L of adsorbent and 10–1000 mg/L Cr(VI) initial concentrations. They also found that the removal efficiency of the PEI–alkali–biochar that exhibited the higher Cr(VI) adsorption capacity was stable at pH 2–7 and then decreased at pH 8–11 [17]. Qu et al. (2022) also studied PEI-modified biochar for Cr(VI) removal from aqueous solutions [58]. Firstly, they prepared biochar from corn stalk powder by pyrolysis at 300 °C. Then, they treated biochar with NH_3 in order to increase the number of PEI grafted onto biochar. Finally, the treated biochar was mixed with PEI in an EDTA, methanol, and deionized water solution. Two PEI–biochar materials were prepared: one was PEI-aminated with the help of a microwave, and the other was at room temperature (25 °C). The first one, PEI–biochar, microwave-assisted, exhibited a maximum adsorption capacity of 155.3 mg/g. The second one, at room temperature, is 120.67 mg/g at pH 2, with the use of 0.5 g/L of adsorbent and 100 mg/L of Cr(VI) initial concentration [58].

It has been found that the modification of activated carbon with PEI improves the selectivity and stability of the adsorbent while also enhancing its ability to absorb. Studies have reported on the use of PEI-modified activated carbon for the removal of chromium from aqueous solutions. Masinga et al. (2022) modified with PEI an activated carbon adsorbent for Cr(VI) removal from aqueous solutions [59]. They added activated carbon derived from Macadamia nutshells to a PEI–methanol solution and put the mixture in a water bath at 80 °C for 24 h. The PEI-activated carbon material exhibited a maximum adsorption capacity of 114 mg/g at pH 2 with a 1 g/L and 200 mg/L Cr(VI) initial concentration [59]. Gao et al. (2023) prepared an adsorbent from polyester fiber, activated carbon powder, and softwood pulp through a wet-forming process. Then, they impregnated PEI by adding the paper-based activated carbon to a mixture of PEI and polyvinyl alcohol in an aqueous solution [60]. The final adsorbent material exhibited an adsorption capacity of 4.96 mg/g at pH 2 with the use of 3 g/L of the adsorbent and 1–15 mg/L of Cr(VI) initial concentrations.

Polyethylenimine-modified cellulose (PEI–cellulose) has shown potential as an effective adsorbent for the removal of chromium from aqueous solutions. Qiu et al. (2014) prepared an adsorbent by mixing a solution of ethylcellulose in ethanol with an ethanol solution of PEI and leaving it to stir at 50 °C [61]. The PEI-modified ethylcellulose exhibited an adsorption capacity of 36.8 mg/g at pH 3 at a dose of 3 g/L for initial Cr(VI) concentrations ranging from 12 to 200 mg/L [61]. Another study by Guo et al. (2017) synthesized PEI-modified cellulose beads by adding the cellulose hydrogel beads to an aqueous PEI solution, and after stirring, an aqueous glutaraldehyde solution was added to the mixture. Finally, the PEI-modified cellulose hydrogel beads were freeze-dried at −50 °C for 12 h after being washed with deionized water. They used various amounts of PEI in the modification process. They found that adsorption capacity increased with increasing PEI content, with a maximum adsorption capacity of 229.1 mg/g for Cr(VI) adsorption onto PEI–cellulose hydrogel beads at pH 2 using 1 g/L of the adsorbent and an initial C(VI) concentration of 10–700 mg/g [62]. Fang et al. (2022) prepared an adsorbent by mixing an aqueous solution of cellulose nanofibers with an aqueous solution of PEI. The mixture was left to stir at room temperature, then polyethylene glycol diglycidyl ether was added, and the final adsorbent was obtained after freeze-drying at −60 °C for 48 h. The authors found a maximum adsorption capacity of 2125.96 mg/g at pH 4.3 with the use of 0.11 g/L of the adsorbent and 150–850 mg/L of Cr(VI) initial concentrations. They also found that the adsorption capacity of PEI–cellulose nanofiber aerogel for Cr(VI) is decreased at pH values greater than 4.3 and higher temperatures [63]. Another study by Pattarith et al. (2023) modified PEI, a cellulose material, by mixing cellulose fibers in dispersion in an aqueous solution with PEI, and the mixture was then heated [30]. The PEI-modified material that was studied for chromium adsorption exhibited a maximum adsorption capacity of 106.6 mg/g for an initial chromium concentration of 100 mg/L and a dose of 0.2 g/L of the adsorbent at 30 °C and pH 3.

The amine groups of PEI can react with the chitosan to form a more stable and mechanically robust adsorbent with a higher adsorption capacity for chromium ions. Li et al. (2017) studied PEI–chitosan aerogel beads as an adsorbent for Cr(VI) from aqueous solutions. They prepared the adsorbent by adding chitosan aerogel beads and PEI in deionized water, then added glutaraldehyde, and the final material was washed with deionized water and ethanol. It was obtained after freeze-drying [64]. The adsorbent showed a maximum adsorption capacity of 402.9 mg/g at pH 2 with the use of 1 g/L and initial Cr(VI) concentrations of 75–500 mg/L. Wang et al. (2021) synthesized PEI-functionalized chitosan aerogel for enhanced Cr(VI) adsorption from an aqueous solution. They mixed an acetic acid solution with the dissolved amount of chitosan and PEI aqueous solution and then added epichlorohydrin as a cross-linking agent. The mixture was left stirring at 60 °C for 4 h to obtain hydrogel. Finally, the hydrogel was freeze-dried for 36 h at −50 °C [65]. PEI-functionalized chitosan aerogel exhibited a maximum adsorption capacity of 445.29 mg/g at pH 3 with the use of 0.2 g/L and 5–145 mg/L of Cr(VI) initial concentrations.

The modification of clays with polyethylenimine (PEI) has been reported to enhance their adsorption capacity and selectivity for chromium ions. Tian et al. (2015) studied PEI-modified halloysite nanotubes for chromium adsorption from aqueous solutions. They modified halloysite nanotubes by first preparing aminopropyltriethoxysilane-modified halloysite nanotubes by adding halloysite nanotube powder to a dry toluene solution of aminopropyltriethoxysilane, and then this material was added to a PEI–methanol solution. The PEI-modified halloysite nanotube material showed a maximum adsorption capacity of 81.5 mg/g at pH 2 with the use of 1.1 g/L of the adsorbents and a 30 mg/L Cr(VI) initial concentration [42]. Fayazi et al. (2020) synthesized PEI-functionalized magnetic montmorillonite clay by adding montmorillonite clay to a ferrous chloride tetrahydrate solution, then adding ammonium hydroxide, and finally PEI to the mixture. The mixture was kept in the oven at 140 °C for 5 h, and the adsorbent was obtained magnetically [40]. The PEI-modified clay exhibited 62.89 mg/g maximum adsorption capacity for Cr(VI) at pH 2 at a dose of 2 g/L and 10–350 mg/L Cr(VI) initial concentrations [40]. Another study by Li et al. (2020) modified PEI with an illite/smectite mixed-layered clay and examined its adsorption capacity for Cr(VI) [66]. For the synthesis of the adsorbent, they mixed illite/smectite nanoflakes and Fe_3O_4 nanoparticles into distilled water, followed by the dropwise addition of a PEI aqueous solution. The mixture was ground in a high-energy density stirred bead mill, and a glutaraldehyde solution was added. The final adsorbent was obtained by a magnet after being washed with deionized water and finally freeze-dried. The composite adsorbent showed a maximum adsorption capacity of 126.6 mg/g at pH 2.3 at a dose of 1 g/L and 10–160 mg/L Cr(VI) initial concentrations [66].

Polyethylenimine can be covalently attached to silica surfaces, increasing the number of available amino groups for complexation with metal ions. The resulting adsorbents exhibit excellent performance in removing Cr(VI) from aqueous solutions. Gao et al. (2009) synthesized PEI-modified silica adsorbent by first preparing silica gel particles activated with methane sulfonic acid in an aqueous solution, then mixing this solution with γ-chloropropyl tri-methoxy silane in xylene at 80 °C for 6 h. The treated silica gel particles were added to a PEI aqueous solution, left stirring at 95 °C for 8 h, and the PEI-modified particles were filtrated and dried under vacuum. The obtained PEI–silica particles were further treated with ethanol, then epihydin as an alkylation agent used for the tertiary amination reaction, and finally benzyl chloride as a quaternization agent. The quaternized PEI–silica particles exhibited a maximum adsorption capacity of 152 mg/g at pH 7 with the use of 0.4 g/L and 10–100 mg/L initial Cr(VI) concentrations [67]. Choi et al. (2018) examined a PEI–silica nanoparticle as an adsorbent for chromium removal from aqueous solutions [68]. They synthesized the PEI–silica adsorbent by mixing PEI aqueous solution with hexadecyl trimethyl ammonium bromide solution. Then, they added tetraethyl orthosilicate reagent to the mixture. Finally, the adsorbent was obtained after centrifugation and rinsing with deionized water. PEI–silica nanoparticles showed 183.7 mg/g maximum adsorption capacity at pH 4 using a dose of 0.5 g/L and initial Cr(VI) concentrations of 10–200 mg/L [68]. Singh et al. (2023) studied another PEI-functionalized silica material for chromium adsorption [69]. They synthesized PEI–silica microspheres by mixing a cetyl trimethyl ammonium bromide aqueous solution with a PEI ethanol solution and a polystyrene suspension mixture, then adding a tetraethyl orthosilicate reagent. The mixture was left to stir for 12 h, and the final material was obtained by centrifugation with deionized water. PEI–silica microspheres exhibited a maximum adsorption capacity of about 57 mg/g at pH 3 with the use of 100 g/L and 1–100 µg/L initial Cr(VI) concentrations [69].

The most efficient polyethylenimine-modified adsorbents for chromate ions that are summarized in Table 2 are PEI–cellulose nanofibers, PEI–chitosan aerogel, PEI-modified alkali–biochar from rice husk, PEI–chitosan aerogel beads, PEI–cellulose hydrogel beads, and PEI–silica nanoparticles. The adsorption process was conducted at pH conditions between 2 and 6.8 for these adsorbents, at which the surface of the adsorbents presents the most positive charge density.

Table 2. Adsorption capacity for Cr(VI) of various PEI-modified adsorbents.

Adsorbent PEI	Adsorbent Dose (g/L)	Adsorption Capacity (mg/g)	pH	Initial Cr(VI) (mg/L)	Ref
PEI-modified acid biochar from rice husk	1	60.78	6.8	10–1000	[17]
PEI-modified alkali–biochar from rice husk	1	435.7	6.8	10–1000	[17]
PEI–biochar from corn stalk powder (microwave-assisted)	0.5	155.3	2	100	[58]
PEI–biochar from corn stalk powder (room temperature)	0.5	120.67	2	100	[58]
PEI-activated carbon derived from Macadamia nutshells	1	114	2	200	[59]
PEI–paper-based activated carbon	3	4.96	2	1–15	[60]
PEI–cellulose	3	36.8	3	12–200	[61]
PEI–cellulose hydrogel beads	1	229.1	2	10–700	[62]
PEI–cellulose nanofibers	0.11	2125.96	4.3	150–850	[63]
PEI–cellulose material	0.2	106.6	3	100	[30]
PEI–chitosan aerogel beads	1	402.9	2	75–500	[64]
PEI chitosan aerogel	0.2	445.29	3	5–145	[65]
PEI halloysite nanotubes	1.1	81.5	2	30	[42]
PEI-magnetic montmorillonite clay	2	62.89	2	10–350	[40]
PEI illite/smectite mixed-layered clay	1	126.6	2.3	10–160	[66]
PEI-modified silica	0.4	152	7	10–100	[67]
PEI–silica nanoparticles	0.5	183.7	4	10–200	[68]
PEI–silica microspheres	100	57	3	1–100	[69]

3.3. PEI-Modified Adsorbents for Arsenic Removal

The adsorption capacity of PEI-based materials for arsenic removal has been reported to be significantly higher than that of other adsorbent materials such as cellulose, chitosan, and silica. PEI-modified cellulose can enhance the arsenic adsorption capacity by providing additional active sites for arsenic binding, improving the surface properties of cellulose, and increasing the electrostatic attraction between cellulose and arsenic ions. One study by Deng et al. (2016) demonstrated the potential of PEI-modified cellulose fibers for the removal of arsenic from water, achieving a high adsorption capacity of 99.35 mg/g for As(V) at pH 4 and 54.13 mg/g for As(III) at pH 7 using a dose of 0.4 g/L and initial arsenic concentrations of 20–250 mg/L [31]. For the adsorbent synthesis, they pretreated cellulose fibers with a sodium hydroxide solution. Then, the pretreated cellulose fibers were mixed with epichlorohydrin and dimethyl sulfoxide for the epoxidation of cellulose fibers. Finally, the treated cellulose fibers were added to a PEI and dimethylformamide solution and left to stir at 115 °C for 15 min. The adsorbent was obtained after being washed with deionized water and dried under vacuum [31]. Another study by Xi et al. (2020) reported the successful modification of cellulose fibers with PEI and their application as an adsorbent for arsenic removal. They achieved a maximum adsorption capacity of 78.71 mg/g for

As(V) and 149.42 mg/g for As(III) at pH 4–6 using 0.4 g/L of the adsorbent and initial arsenic concentrations of 20–300 mg/L at pH 4 [70]. They extracted cellulose nanocrystals from raw kapok fiber by TEMPO oxidation [71]. Cellulose nanocrystals were mixed with a PEI solution, and then a Fe(III) solution was added to the mixed solution in a water bath at 40 °C. After the addition of NH_3 and pH adjustment, the final adsorbent material was obtained, washed with deionized water, and vacuum dried [70].

Polyethylenimine-modified chitosan has been reported as an effective adsorbent for arsenic removal from water. Alsaiari et al. (2021) reported the synthesis of a magnetic polyethylenimine-modified chitosan composite and demonstrated its adsorption capacity for both As(III) and As(V) species [72]. They synthesized the composite material by first preparing the magnetic Fe_3O_4-chitosan nanoparticles, and then modification with PEI took place by mixing the magnetic nanoparticles with PEI solution for 5.0 h at 90 °C. The final Fe_3O_4–chitosan–PEI nanocomposite material was obtained after being washed with deionized water and dried at 65 °C. It showed a maximum adsorption capacity of 86.5 mg/g for As(V) and 77.61 mg/g for As(III) at pH 6.7 using a dose of 1.5 and 2 g/L, respectively, and 10–500 mg/L of initial arsenic concentrations [72]. Similarly, Li et al. (2021) synthesized magnetic chitosan by mixing chitosan with $FeCl_2$–$FeCl_3$ solution and epichlorohydrin as a cross-linked reagent. The obtained magnetic material was added to a mixture of graphene oxide, EDC, and N-hydroxysuccinimide solution, stirred at 60 °C, and then PEI was added for further graphene oxide and PEI modification. The magnetic chitosan nanocomposites modified by graphene oxide and polyethyleneimine exhibited a maximum adsorption capacity of 220.26 mg/g at pH 7 at a dose of 0.5 mg/L and 25–300 mg/L initial arsenic concentrations [73].

A polyethylenimine-modified silica-based adsorbent for arsenic removal from water was examined by Yohai et al. (2020) [74]. These authors synthesized mesoporous silica material by hydrolytic condensation in basic media. Next, the silica nanoparticles are activated with acid. The activated silica nanoparticles were added to the glutaraldehyde solution, followed by the addition of water, and the mixture was stirred at room temperature. After washing and drying the obtained nanoparticles, they were mixed with a PEI aqueous solution at 50 °C. The resulting mixture was then washed with deionized water and vacuum dried. After the modification of silica nanoparticles with PEI, they were cross-linked with polyacrylonitrile membranes by orbital shaking in deionized water. Finally, the nanocomposites were immersed in an ethanol solution of iron(III) nitrate to incorporate Fe^{3+}. The adsorption capacity of the nanocomposite membranes for As(V) was 5.89 mg/g at pH 8 at a dose of 2 g/L and As(V) initial concentration of 1 mg/L [68].

The most efficient polyethylenimine-modified adsorbents for arsenate ions, which are presented in Table 3, are PEI-magnetic chitosan GO nanocomposite, PEI–cellulose fibers, and magnetic PEI–chitosan composite. These adsorbents exhibited higher adsorption capacities at neutral pH.

Table 3. Adsorption capacity for As(V) of various PEI-modified adsorbents.

Adsorbent PEI	Adsorbent Dose (g/L)	Adsorption Capacity (mg/g)	pH	Initial As (mg/L)	Ref
PEI–cellulose fibers	0.4	99.35	7	20–250	[31]
PEI–cellulose nanocrystals from raw kapok fiber	0.4	78.71	4–6	20–300	[70]
Magnetic PEI–chitosan composite	21.5	86.5 As	6.7	10–500	[72]
PEI-magnetic chitosan GO nanocomposites	0.5	220.26	7	25–300	[73]
PEI-mesoporous silica	2	5.89	8	1	[74]

4. Discussion on Enhanced Adsorption Performance

The performance of adsorbents can be enhanced by modifying their surface properties, and one such modification involves the incorporation of polyethylenimine (PEI). This discussion aims to compare the results of adsorbents with and without PEI, evaluate their adsorption performance, and highlight the influence of PEI on adsorption capacity.

Concerning chromium adsorption, the modification with PEI enhanced the capacity of the adsorbents for a few hundred units, with the maximum being found for PEI–cellulose material from 12.5 to 30 mg/g to 2125 mg/g. Biochar and chitosan modification with PEI showed an increase in capacity from 4.72 to 23.09 mg/g and 23.4 to 76.92 mg/g, respectively, to a maximum of about 400 mg/g. PEI-modified activated carbon and clays showed an increase from about 45 and 59 mg/g, respectively, to over 100 mg/g. In comparison, PEI-modified silica showed an increase in capacity from 4.6 mg/g to a maximum of 183 mg/g.

The modification with PEI also enhanced the adsorption capacity towards arsenic, but at a lower level compared to chromium capacity. The maximum adsorption capacity for arsenic, achieved through the modification with PEI, was found to range from 33.87 to 220 mg/g for the chitosan materials. Cellulose and silica modification with PEI showed an increase in the capacity for arsenic from 5 to 10 mg/g and about 0.5 mg/g to a maximum of 99 and 89 mg/g, respectively.

The incorporation of polyethylenimine (PEI) in adsorbents offers potential advantages in terms of enhanced adsorption capacity. However, a comprehensive comparison with unmodified adsorbents is essential to evaluating the true benefits and limitations of PEI modification. By analyzing the adsorption capacity and considering practical applications and cost considerations, we can gain insights into the overall performance and viability of adsorbents with and without PEI. Such knowledge will aid in developing optimized adsorbents for specific environmental remediation applications.

5. Conclusions

The modification of adsorbents with polyethylenimine can provide several benefits for adsorption applications. PEI modification can significantly increase the adsorption capacity of adsorbents for chromate and arsenate ions. The amino groups of PEI can form electrostatic interactions with the anionic species, leading to improved adsorption efficiency. This modification introduces additional active sites on the adsorbent surface, increasing the number of binding sites available for ion adsorption. PEI-modified adsorbents often exhibit increased pH tolerance compared to unmodified adsorbents. The cationic nature of PEI allows it to adsorb anions over a broader pH range, including acidic and neutral conditions. This is beneficial as it enables the effective adsorption of chromate and arsenate ions from diverse water sources with varying pH levels. PEI modification can enhance the selectivity of adsorbents towards chromate and arsenate ions. The electrostatic attraction between the positively charged amino groups of PEI and the anionic species facilitates preferential adsorption of these contaminants over other co-existing anions in the solution. Also, the reversible nature of the electrostatic interactions between PEI and the adsorbed ions allows for the desorption of the contaminants under appropriate conditions, making the adsorbent available for subsequent adsorption cycles.

PEI is known for its stability and compatibility with different adsorbent matrices. It can be easily immobilized or coated onto various support materials, such as biochar, activated carbon, or silica, without significant loss of its adsorption properties. This versatility makes PEI modification a feasible approach for enhancing the performance of different adsorbents.

In research and industrial applications, scientists and engineers often explore different raw materials and process conditions to develop adsorbents that are more effective and tailored to specific requirements. It is important to consider the specific adsorption needs of a given application when selecting an adsorbent material, as different materials may exhibit vastly different performances for different substances. Regarding the adsorbent materials that are more effective than other same-based materials, it seems that it depends on the raw material that they are derived from. Chitosan adsorbents seem to be the most effective for both chromate and arsenate ions due to their positive surface charge related to their amino group content. Concerning the PEI-modified materials, PEI–cellulose nanofibers seem to be more efficient for chromate ions and PEI-magnetic chitosan nanocomposites for arsenate ions.

Overall, the modification of adsorbents with PEI offers the potential for improved adsorption capacity, pH tolerance, selectivity, regeneration, and stability. This modification can enhance the effectiveness of these materials for the removal of chromate and arsenate ions from water sources. However, it is important to optimize the PEI loading and consider the specific application requirements to maximize the benefits of this modification.

Author Contributions: Conceptualization I.A.K.; methodology, I.A.K. and M.X.; writing—original draft preparation, M.X.; writing—review and editing, I.A.K. and M.X.; supervision, I.A.K.; project adminiration, I.A.K. All authors have read and agreed to the published version of the manuscript.

Funding: This research work was supported by the Hellenic Foundation for Research and Innovation (HFRI) under the 4th Call for HFRI PhD Fellowships (Fellowship Number 11052).

Data Availability Statement: No new data were created.

Conflicts of Interest: The authors declare no conflict of interest.

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