

Review

Wastewater Treatment Utilizing Industrial Waste Fly Ash as a Low-Cost Adsorbent for Heavy Metal Removal: Literature Review

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Abstract: Wastewater discharges from industrial processes typically include elevated concentrations of contaminants, which largely consist of potentially harmful chemicals such as heavy metals. These contaminants are characterized by their slow rate of decomposition. Hence, the removal of these metallic ions from effluents poses a challenge. Among different treatments, the adsorption approach has considerable potential due to its ability to effectively eliminate both soluble and insoluble pollutants from effluent, even at lower levels of concentration. Of various wastes, fly ash (FA) material has been the subject of attention because it is abundant, has favorable qualities, and contains a high percentage of minerals. This review investigates multiple facets, with a specific focus on the application of FA, an industrial byproduct, as an adsorbent in removing heavy metals. A comprehensive examination was conducted on a range of concerns pertaining to the pollution caused by metallic ions, including the underlying causes, levels of contamination, health implications of heavy metals, and removal methods. Multiple factors were found to affect the adsorption process. Of all the factors, the pH value considerably influences the elimination of heavy metals. An acidic pH range of 2.5–4.5 was found to be optimal for achieving the highest possible elimination of As(V), Cu(II), Hg(II), and Cr(VI). The latter elimination rate reached 89% at the optimal pH level. Most heavy metals' adsorption isotherms conformed to the Langmuir or Freundlich models, while the pseudo-second-order kinetics provided a satisfactory match for their removal. Using a raw FA, adsorption capacities were achieved in the removal of metallic ions, Ni(II), Pb(II), and Cr(VI), that ranged from 14.0 to 23.9 mg g⁻¹. Meanwhile, the FA-zeolite showed a remarkable capacity to adsorb ions Mn(II), Ni(II), Cd(II), Cu(II), and Pb(II), with values ranging from about 31 to 66 mg g⁻¹. The cost analysis showed that the treatment of FA is economically advantageous and may result in significant cost reductions in comparison to commercial adsorbents. In summary, FA is an inexpensive waste material with potential for water treatment applications and several other purposes due to its excellent chemical and mineralogical composition.



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1. Introduction

Wastewater treatment plays a crucial role in protecting public health, preserving the environment, and ensuring the sustainable use of water resources. Wastewater contains various pollutants, including harmful microorganisms, chemicals, and other contaminants. If wastewater is left untreated, these pollutants can pose significant risks to public health. Wastewater treatment removes and/or reduces these contaminants, ensuring the water is safe for disposal or reuse. This results in minimizing the spread of waterborne diseases and protecting public health [1–3]. Untreated and/or poorly treated wastewater has significant negative impacts on ecosystems and water bodies. It can introduce excess nutrients like nitrogen and phosphorus into water bodies, leading to eutrophication, oxygen depletion,

and the disruption of aquatic ecosystems. Therefore, effective wastewater treatment helps to mitigate these adverse effects and preserve the integrity of natural ecosystems [4–6].

As freshwater resources become increasingly scarce, wastewater treatment also plays a vital role in water resource management. Treated wastewater, also known as reclaimed or recycled water, has the potential to be repurposed for diverse uses, including irrigation, industrial operations, and as a source of drinkable water. By treating and reusing wastewater, water availability can be enhanced, reducing the strain on freshwater sources and promoting sustainable water management practices [7–9]. In addition, many countries have regulations and standards to ensure proper wastewater management and treatment. Compliance with these regulations is essential for industries, municipalities, and other entities that generate wastewater. Adequate wastewater treatment helps these entities meet regulatory requirements, avoid penalties, and maintain their social and environmental responsibilities [10–13]. Furthermore, proper wastewater treatment aligns with the principles of sustainable development. Treating wastewater can minimize pollution, protect ecosystems, and conserve water resources for present and future generations. It promotes the efficient use of water resources, reduces environmental impacts, and supports social and economic development in a sustainable manner [14–17].

Moreover, wastewater treatment plays a vital role in supporting the principles of a circular economy [1]. The circular economy is a framework designed to promote the extended retention of products, substances, and resources within the economic system, maximizing their lifespan and minimizing waste. In the circular economy context, waste is recognized as a valuable resource that must be repurposed and reintegrated into the economy for further utilization as secondary raw substances [18–20]. The involvement of wastewater treatment plants in the circular economy stems from their capacity to effectively extract nutrients, reuse water, and harness energy resources, making a valuable contribution to the sustainable resource cycle [21–23].

For all the reasons mentioned above, the wastewater treatment topic has attracted significant attention from scientists and engineers in the water sector, academic institutions, and environmental protection agencies over the recent decades. The main advantages of the wastewater treatment approach are highlighted in Figure 1.

Environmental contamination, a global issue caused by the release of industrial effluents containing harmful heavy metals, has led to the contamination of water sources. The primary causes of heavy metal ion pollution are mining operations, electrolysis, textile production, battery making, tanning factories, refinery operations, painting and pesticide production, and the printing industry [24,25]. In contrast to other pollutants, metallic ions exhibit non-biodegradable properties and have an accumulation tendency inside living beings. Most metallic ions have been identified as possessing hazardous and carcinogenic properties. Thus, regulating and monitoring heavy metal levels in effluents have a particular significance [26,27].

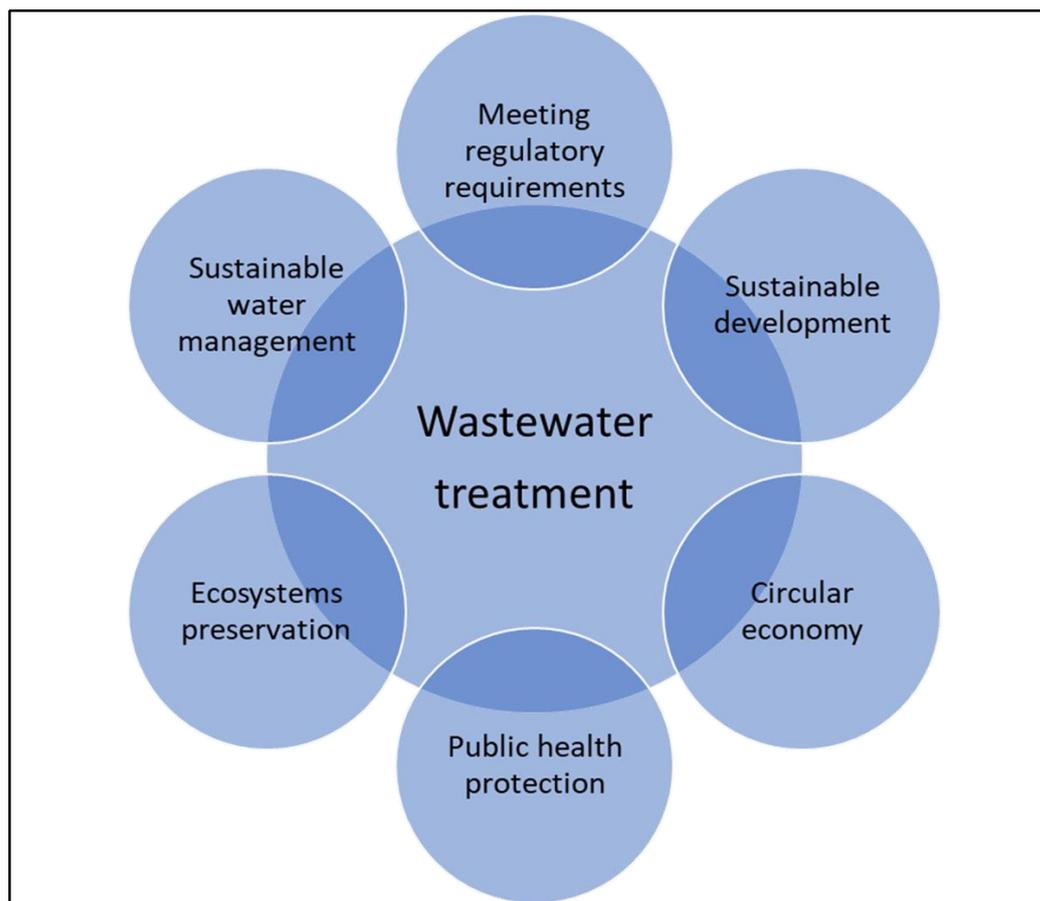


Figure 1. Major benefits of the wastewater treatment approach.

Numerous procedures, including precipitation with chemicals, extraction, electrochemical processes, ozonation, filtration via membranes, reverse osmosis, coagulation, and advanced oxidation, have been used to remove hazardous metallic ions from wastewater solutions [28–33]. Nevertheless, it is essential to acknowledge that these procedures include some drawbacks. On the other hand, the adsorption method has shown great promise since it can efficiently remove both soluble and insoluble contaminants in wastewater, even at lower concentrations [34]. A number of traditional materials, such as activated carbon, zeolites, and alumina, have been effectively employed for the purpose of water purification, which includes the removal of heavy metals [35–40]. Most of the mentioned adsorbents possess exceptional characteristics, such as high efficacy, polarity, and a substantial surface area, which enable them to effectively eliminate various pollutants, such as organic compounds, inorganic ions, and heavy metals [41,42]. The majority of such adsorbents have better adsorption capabilities after surface modification, which involves chemical or physical treatment [42,43]. Nevertheless, the substantial cost of utilizing all the mentioned materials appears to be their main drawback [42,44]. Moreover, significant activation expenses and limited potential for reusability pose significant obstacles to the utilization of such substances, particularly activated carbon. Nevertheless, they are often used as an adsorbent material for a variety of applications [42,45]. Activated carbon, derived from organic substances' carbonization process, is considered the most common adsorbent. Activated carbon has shown favorable capabilities for adsorbing metal ions [46–48]. The removal of heavy metals from wastewater has been accomplished using a number of different forms of activated carbon, such as powdered and granulated activated carbon. Studies have shown that activated carbon has a strong ability to remove metallic ions because of its high adsorption capability. However, its capacity varies based on the

kind of activated carbon used, its activation treatment, and the type of heavy metal ion being removed [49,50].

In addition, different natural-based adsorbents have been used as adsorbents. Such adsorbents are easily obtainable substances in enormous quantities. These materials possess several attributes, such as a significant capacity for cation exchange and a large surface area, which are essential qualities for adsorbents. Furthermore, their pricing is much more affordable in comparison to traditional adsorbents [51]. These adsorbents consist of a wide variety of materials, including clays and zeolites, among others. Extensively studied, clinoptilolite, a natural zeolite, has shown remarkable selectivity in removing several heavy metals, such as Cu(II), Zn(II), and Cd(II). Furthermore, the pretreatment method was revealed to impact the clinoptilolite's capability for ion exchange. Consequently, this pretreatment improves not only the characteristics of the clinoptilolite but also its efficacy in eliminating substances [52–54]. Mineral clay is yet another natural substance that has the ability to absorb compounds and ions. Clay may be classified into three basic groups: bentonite, mica, and kaolinite. Among these categories, bentonite possesses the highest cation exchange capability, exceptional selectivity, and significant potential for reusability. Additionally, its material is more cost-effective than activated carbon [55]. These substances have a reduced capability to eliminate metallic ions compared to zeolites, which have a better capacity. However, due to their many advantages compared to traditional adsorbents, these substances are used to eliminate different heavy metals from polluted effluents. These properties include a significant surface area, acceptable structural properties that resist corrosion and chemical actions, as well as exceptional physical and chemical characteristics such as a strong binding force and high capability for ion exchange [56–58]. Much research has utilized clay without surface treatment to remove metallic ions from wastewater [59–61]. By incorporating a polymeric material, it is possible to significantly boost its capability for the removal of heavy metals. Such incorporation results in the formation of a clay–polymer adsorbent substance [62,63]. In addition, the calcination method has been used in a significant number of studies for clay modification before its usage in removing metallic ions. This method involves subjecting clay to high temperatures, often above 250 °C, for a certain duration before use [64,65]. An alternative method for removing metallic ions is using acidic treatment to modify the clay surface. The clay surface is subjected to acid treatment using acids like H₂SO₄ and HCl. Subsequently, the clay is subjected to NaOH treatment to eliminate the acidic impact [66,67].

In recent years, there has been a significant increase in the number of attempts aimed at evaluating the efficacy of inexpensive adsorbents in the removal of metallic ions. Numerous researchers have examined different waste types, including industrial waste, focusing on their qualities of adsorbing heavy metals [68]. Fly ash (FA) material has been focused on among different waste types due to its large abundance, good properties, and high mineralogical content. In the decades after the introduction of large-scale coal-fired power plants in the 1920s, significant amounts of ash and other associated by-products connected to coal combustion have been generated [69]. Nowadays, the use of coal as a fuel source is substantial all over the globe. Coal-fired power plants are the primary source of electricity generation in the majority of nations, and they are responsible for around 40% of the total electricity output globally [70,71]. Annually, power generation consumes approximately 80% of coal, leading to the production of huge amounts of FA as a by-product of coal combustion. These tremendous amounts were estimated to be 686, 715, and 748 Mt annually during the period between 2017 and 2019 [72]. Therefore, insufficient management of this considerable volume of industrial refuse could potentially result in severe environmental consequences. The main source of FA is power generation units, which produce it as a by-product resulting from coal burning. As shown in Figure 2, various by-products are generated due to coal burning. However, FA is considered the main by-product of coal combustion.

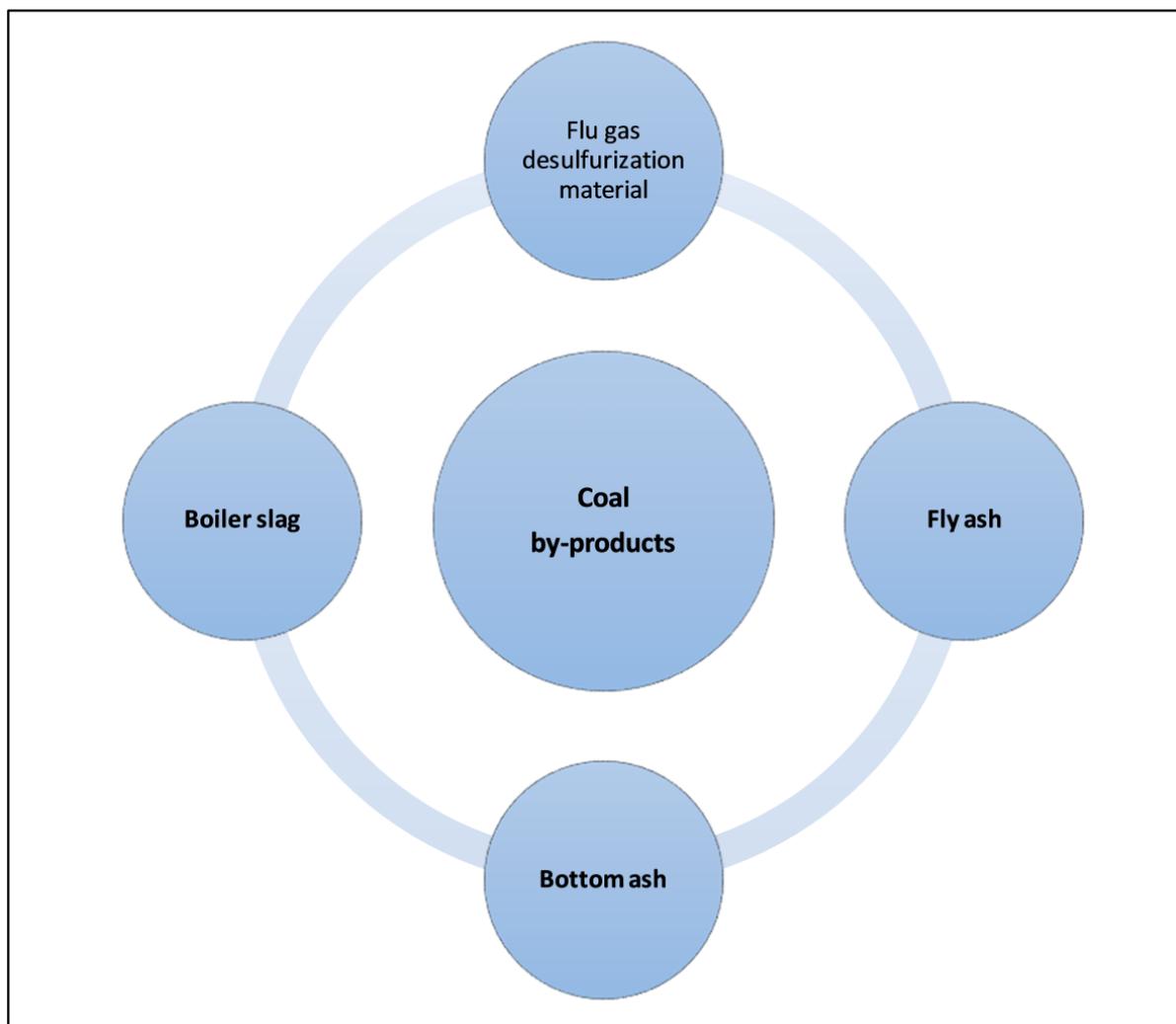


Figure 2. Different by-products generated from coal burning; the by-product classification was taken from [73].

From the standpoint of electricity production, FA is considered residue waste; however, from the viewpoint of coal utilization, FA represents an untapped resource with significant potential for further development and use [70]. Due to this waste's environmental and economic significance, extensive global research has been conducted to investigate the possibility of reusing it and making the most of its potential applications. Thus, the use of FA as a resource has been explored in several sectors, including the building industry, agriculture activities, and environmental protection domains, where it has been utilized as an alternative option to cement in the concrete industry [74]. For instance, approximately 20% of the FA produced is utilized in manufacturing concrete [75]. Additionally, there have been endeavors to use FA as a fertilizer and cleaning material for exhaust gas treatment, and to apply it in the domains of soil amendment and mining backfill [76–78]. Nevertheless, the implementations mentioned above fail to fully exploit the potential of the FA that is produced. Based on the American Coal Ash Association (ACAA), a total of slightly higher than 53 million tonnes of FA was generated in 2013, of which only slightly more than 23 million tonnes were utilized. Therefore, the entire FA utilization rate only accounted for 43.5%, and the remaining waste was disposed of in landfills, resulting in significant issues for the environment and the economy [79].

Given its importance and the strong likelihood of practical usage, several evaluations have thoroughly concentrated on the applications of FA. A few of them are located in [75,80]. Instead of directing their attention toward broad applications, several reviewers have chosen to concentrate on particular uses of FA. A group explored the potential for FA production in manufacturing high-value materials such as geopolymers and ceramics, their derivatives like glass–ceramic, and their different applications, including thermal insulation and ceramic membranes [70,72]. On the other hand, some research has examined the characteristics and characterization of FA as a material [73]. Related to this, Hower et al. [81] have extensively examined unburned carbon in FA material in terms of different aspects, such as the determination of unburned carbon and its classification, the influence of parameters on the unburned carbon amount, and the unburned carbon variance and its relation to coal type and rank. Some studies have evaluated using FA as an adsorbent in flue gas cleaning (sulfur and NO_x compounds), dyes and organic compounds, inorganic anions, and heavy metal ions [69]. For instance, Aigbe et al. [82] reviewed using FA as an adsorbent for removing heavy metals as part of their study, along with eliminating organic dyes. In the mentioned review, while many useful things were discussed, some aspects regarding heavy metals were not covered, such as removal approaches for heavy metals, cost analysis of FA material compared to other adsorbents, and future perspectives of FA material. Meanwhile, other research has discussed the removal of specific heavy metals, Hg and As, from flue gas and water using FA material [83]. Similarly, other researchers assessed the removal of heavy metals using FA or FA-based zeolite, both generated from municipal solid waste [84,85]. Based on the above discussion, it can be stated that most research has focused on different aspects of FA, including its properties and applications. Although there have been studies that dealt with heavy metal removal using FA as an adsorbent, the existing literature studies have three directions: FA generated from a specific origin (e.g., MSW), a focus on removal of a particular heavy metal, and the discussion of heavy metal removal as part of an extensive assessment. Thus, there is a need for a critical review that deals with heavy metal removal using FA as an industrial waste to cover different related aspects.

The primary objective of this review paper is to summarize the relevant literature on using FA, an industrial waste, as an adsorbent for removing heavy metals from wastewater. The paper also provides critical analysis from diverse standpoints, including adsorption process variables, the influence of FA constituents, and the effects of introducing additional materials on FA performance. Further dimensions are addressed, including removal isotherms, kinetics, and adsorption capability. This review also discusses various issues related to the contamination of metallic ions, covering factors behind pollution, contamination levels, health consequences of heavy metals, and strategies for their removal. A cost analysis, including a comparison of FA price with different adsorbents and cost savings of FA usage compared to using various adsorbents, is also discussed in this paper.

2. Causes of Heavy Metal Pollution

Water pollution primarily arises from inadequately treated sewage water, harmful industrial contaminants, industrial wastewater, and agricultural runoff [42,86]. Out of these factors, industrial wastewater is widely acknowledged as a primary contributor to causing water pollution [87,88]. Industrial effluents tend to exhibit higher levels of pollutants than other forms of wastewater, specifically containing hazardous substances like heavy metals. These pollutants are considered extremely toxic and possess limited degradability [89]. Discharging even small amounts of such harmful effluents into water poses a grave threat to aquatic ecosystems and their inhabitants, leading to substantial disturbances and significant damage [90].

Meanwhile, economic progress relies on urbanization, industrialization, and rapid population expansion. Nevertheless, these factors have detrimental consequences on diverse ecosystems, such as water bodies, air quality, and the overall health of the earth's inhabitants [91–93]. Industries such as refineries, plastics manufacturing, chemical production, and battery plants consistently pollute a variety of water sources (e.g., rivers) [94,95]. In addition, the inclusion of metallic ions is commonly necessary for factories like tanneries, electrical industries, and metal plating as an essential element of their operational procedures [95–98]. Thus, as the factories and human-associated endeavors have progressed, there has been a corresponding escalation in the concentrations of heavy metals found in industrial wastewater. Such progress includes different sources of heavy metals: electrolysis processes, mining activities, the paper manufacturing sector, the fertilizer industry, and pesticides [95–97]. Consequently, significant quantities of wastewater containing metals have been released into the environment as a result of the activities undertaken by these industries [99–102]. Apart from polluting water bodies, the seepage of heavy metals during rainfall and snowfall in minute amounts can also contaminate groundwater [103,104]. The industrial wastewater from the activities mentioned above contains heavy metals, and among them, elements such as cadmium (Cd), nickel (Ni), arsenic (As), mercury (Hg), and lead (Pb) are known to exhibit significant levels of toxicity [104–107]. Heavy metals constitute a substantial portion of pollutants found in soil and water, giving rise to toxicity [108]. Heavy metals are present in diverse ecosystems, such as soil and water, posing a risk of contaminating both food and potable water sources [104]. As a result, significant global apprehension has emerged regarding the environmental discharge of heavy metals, precisely due to their detrimental impact on water quality [94].

3. Concept of Heavy Metals

Heavy metals typically denote a collection of dense and toxic elements, which can have detrimental effects even when present in extremely low concentrations [109,110]. This category encompasses metals and metalloids characterized by densities surpassing 5 g cm^{-3} with atomic masses spanning a range of approximately 60 to 200 [100,102,111–113]. Examples of such metals include chromium (Cr), copper (Cu), and zinc (Zn). These elements are commonly found in different water environments, with concentrations normally ranging from nanograms to milligrams per liter [114–116].

Heavy metals enter ecosystems through two distinct pathways: one originating from natural sources and the other resulting from human-related activities, which are also known as anthropogenic actions. Heavy metals are released into the environment through natural mechanisms such as volcanic eruptions, soil degradation, and the breakdown of rocks [91,111,117]. It is known that igneous rocks constitute around 95% of the Earth's crust, whereas sedimentary rocks make up roughly 5% of the total composition [118]. Typically, Cd, Co, Ni, and Cu are prevalent heavy metals found in basaltic igneous rocks, while shales are usually characterized by substantial quantities of Mn, Pb, and Zn [119]. In addition, air pollution and river sediment are recognized as the predominant factors responsible for the pollution of heavy metals in coastal environments [120]. Human activities encompass various industrial operations like the mining industry, chip production, pesticides and fertilizers, metal purification, the steel industry, and dye manufacturing, along with runoff, waste disposal, and agricultural practices [94,111,120–122]. Thus, heavy metals have gained significant prominence as highly prevalent toxic elements found in different environments [111,123]. Table 1 provides a comprehensive list of the heavy metals found in wastewater discharged by various industrial sectors.

Table 1. Types of heavy metals in wastewater released by different industries.

N	Industry Sector Type/Process	Heavy Metals That Released from Different Sources														Ref.	
		Al	As	Cd	Co	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Sb	Se	Zn		
1	Aircraft manufacturing	×		×		×	×	×			×						[124]
2	Blast furnace							×		×						×	[125]
3	Chemicals production		×	×		×	×	×			×	×				×	[126]
4	Coal burning			×										×			[125]
5	Distillery			×		×	×					×			×		[127]
6	Dairy industry			×			×	×				×			×		[128]
7	Dyes manufacturing			×		×	×	×			×	×			×		[129]
8	Electrolysis processes								×								[125]
9	Electroplating process			×												×	[130]
10	Engineering industry			×		×	×	×			×	×				×	[129]
11	Fertilizers industry	×	×	×		×	×		×		×	×				×	[124]
12	Fine chemicals industry			×		×	×	×			×	×				×	[129]
13	Food additives industry						×									×	[125]
14	Food industry			×		×	×					×				×	[128]
15	High-tension lines manufacturing						×									×	[125]
16	Household waste			×			×				×	×				×	[125]
17	Metal smelting			×			×				×	×				×	[125]
18	Oil refinery	×	×	×		×	×				×	×				×	[124]
19	Organic chemistry	×	×	×		×			×			×				×	[124]
20	Paper mill			×		×	×	×	×	×	×	×				×	[124,129]
21	Pesticides industry		×	×			×		×			×					[125,130]
22	Petroleum combustion										×						[125]
23	Petroleum industry			×		×	×					×				×	[131]
24	Pharmaceuticals industry		×	×		×	×				×	×				×	[132]
25	Plastic manufacturing			×		×			×			×	×				[133]
26	Pulp and paper industry			×		×	×					×				×	[134]
27	Steel manufacturing		×	×	×	×	×		×		×	×				×	[124]
28	Soap and detergents			×		×	×	×		×		×				×	[135]
29	Sugar industry		×	×		×	×		×			×					[136]
30	Tanning industry		×	×		×	×					×				×	[137]
31	Textile and dyeing		×			×	×	×	×		×					×	[138]
32	Wastewater sludge			×			×				×	×				×	[125]

4. Levels of Heavy Metal Pollution

The presence of metallic ions in the environment poses a significant concern due to their detrimental effects [94,106,139,140]. Even in small amounts, these metals are highly hazardous substances due to their notable carcinogenic properties and capacity for accumulation [55,92,98,141]. The primary cause of accumulation in various organisms is primarily attributed to the non-degradable nature of these metals [94,142,143]. In addition, heavy metals exhibit high solubility in aquatic environments, facilitating their absorption by various species. Consequently, when these metals enter into food chains, they have the potential to accumulate in substantial amounts, leading to grave repercussions for organisms [144–146]. The non-degradability and strong stability of metallic ions contribute to their adverse impact on environments in terms of waste problems.

Even through biological degradation processes, these metals remain persistent and resistant to breaking down, posing a significant environmental danger [101,147]. Hence, the growing global focus on water decontamination by heavy metals is understandable, given the significant dangers it presents to various living things and its adverse impact on the environment [141,146,148–150]. The presence of heavy metal pollution, even in minute quantities, could impose substantial damage to diverse forms of life. Consequently, it becomes crucial to effectively eliminate metallic ion contaminants from polluted water [98,122,151]. To achieve this, environmental agencies and scientific centers have established guidelines and defined specific thresholds for metallic ions' presence in drinking water. These thresholds, subject to regular revisions, indicate the maximum acceptable levels of contaminants and are commonly referred to as maximum contamination levels (MCLs) [122,152]. The specified levels of MCL values for different heavy metals, as established by multiple countries, are presented in Table 2.

Table 2. MCL values for heavy metals in drinking water established by different countries.

N	Metal	MCL Values ¹			
		US ²	Canada ³	UK ⁴	WHO ⁵
1	Al	0.2	0.1	0.2	-
2	Ag	-	-	-	-
3	As	0.01	0.01	0.01	0.01
4	B	-	5.0	1	2.4
5	Ba	2.0	2.0	-	0.7
6	Be	0.004	-	-	-
7	Cd	0.005	0.007	0.005	0.003
8	Cr	0.1	0.05	0.05	0.05
9	Cu	0.25 *	2.0	2.0	2.0
10	Fe	-	-	0.2	-
11	Hg	0.00003	0.001	0.001	0.006
12	Mn	-	0.12	0.05	-
13	Ni	0.2 *	-	0.02	0.07
14	Pb	0.006 *	0.005	0.01	0.01
15	Sb	0.006	0.006	-	0.02
16	Se	0.05	0.05	0.01	0.04
17	U	0.03	0.02	-	0.03
18	Zn	0.8 *	-	-	-

Remarks: ¹. All MCL values in this table are presented in mg L⁻¹. ². The US/EPA guide values were taken from [153]. ³. The Canadian guide values were acquired from [154]. ⁴. The UK guide represents the values set by the Drinking Water Inspectorate (DWI)/Department for Environment, Food, and Rural Affairs (DEFRA). ⁵. The WHO values were taken from [155]. * These values were obtained from other sources [98,99,111].

5. Health Effects of Heavy Metals

Ecosystems face a significant danger as vast quantities of harmful heavy metals are released into the environment through industrial wastewater from various sectors like electrolysis units, metal plating, and pigment production. This discharge of hazardous substances poses a substantial risk to the health of humans, organisms, and the delicate balance of ecosystems [101,113,156]. Heavy metals tend to induce genotoxic effects, with both immediate and persistent toxic repercussions, adverse impacts on development and reproduction, and the potential to cause cancer in different organisms [114,157,158]. Industrial wastewater from different activities contains a range of heavy metals, including but not limited to As, Cd, Cr, Cu, Hg, Ni, and Pb, which have demonstrated a significant degree of toxicity [94,107,122]. Among them, Cd, Hg, and Pb are widely known as the most hazardous, primarily due to their considerable ecological consequences [159].

In addition, Pb and Cd exhibit a high level of toxicity toward the neural system, acting as neurotoxic agents. Furthermore, elements such as As, Cr, Cu, Mn, and Zn are also recognized as substances with poisonous properties [160]. In terms of toxicity to humans, however, the metallic ions can be ranked (high to low level) in the following order: Hg > Cd > Pb > Cr > Ni > Mn > Cu > Fe > Zn [113,161]. When heavy metals enter the human body and accumulate to surpass the permissible limit, they pose a significant threat to living organisms. However, some metallic ions, including Cd and Ag, exhibit high toxicity levels, even in minute amounts [139]. The potential signs of toxic metals encompass a range of symptoms, including hypertension, speech impairments, sleep disturbances, aggressiveness, difficulties with concentration, mood fluctuations, heightened allergic reactions, arterial blockage, and cognitive decline [162]. In addition, the presence of metallic ions can lead to long-lasting disruptions in physiological systems, muscle pain, and possibly fatal illnesses [99,163]. Furthermore, metallic ions can profoundly impact the neural system, resulting in substantial impairment. They can also lead to a decrease in energy levels, modify blood components, and inflict harm upon vital organs such as the kidneys and lungs [164,165]. A detailed explanation of the detrimental health impacts caused by different heavy metals on humans is provided in Table 3.

Table 3. Adverse health effects resulting from various heavy metals and metalloids on humans.

N	Metal	Health Hazards Resulting From Exposure To Heavy Metals	Ref.
1	Ag	Lowered blood pressure, diarrhea, gastric irritation, and reduced breathing; occurrence of fatty degeneration in the kidneys and liver along with modifications in blood cell composition.	[166]
2	As	It specifically affects the outer layer of the skin, resulting in damage and potentially leading to the onset of skin cancer in its later stages; diverse complications involving the circulatory system, including arterial issues and the presence of diabetes; cancerous conditions involving the skin, lungs, and kidneys, as well as other internal malignancies; the potential for increased infant mortality and lower birth weight in newborns; neurological issues; developmental challenges, neurobehavioral disorders, blood-related conditions, and genotoxic effects.	[94,99,104]
3	B	Headaches, lowered body temperature, fatigue, kidney problems, skin inflammation, hair loss, loss of appetite, and digestive disorders.	[167]
4	Ba	Increased blood pressure levels	[153]
5	Be	Digestive disorders	[153]
6	Cd	Various complications affect the kidneys, resulting in damage, severe bone pain, liver disorders, hypertension, and a substantial risk of cancer development.	[99,101,106,168]
7	Co	The primary organs affected are the respiratory system and skin, with the possibility of developing hypersensitivity lung disease leading to irreversible fibrosis as well as dermatitis caused by a reaction of inflammation.	[169–171]
8	Cr	Symptoms of nausea and significant diarrhea, obstruction of the lungs, and impairment of liver and kidney functions; a substance with nephrotoxic properties with a high likelihood of causing cancer; and it has an association with disorders of the skin, nervous system, and digestive system, as well as the development of malignancies in different organs like the lungs and thyroid.	[172–174]
9	Cu	Short-term effects may include hypertension, sleeplessness, rapid respiration, seizures, and muscular cramps; a tendency to accumulate in different areas, including the skin and brain, giving rise to significant toxic implications that can ultimately result in long-term harm, particularly to the kidneys and liver; occurrence of Wilson’s disease and Menkes syndrome.	[94,106,175–177]

Table 3. Cont.

N	Metal	Health Hazards Resulting From Exposure To Heavy Metals	Ref.
10	Hg	In the immediate term, it primarily targets the neurological system, causing significant damage to the central neural system and exhibiting nephrotoxic effects; over the long term, it can have severe implications on multiple organs, particularly brain and kidneys, as well as various bodily systems like immune and respiratory; and it is linked to neurodevelopmental challenges, encompassing conditions such as tic disorders and delayed speech.	[94,178–180]
11	Mn	The central neurological system is the primary organ affected by the Mn toxic effects. Chronic exposure to Mn leads to alterations in neurological and neurobehavioral functions. Neurobehavioral signs encompass changes in mood, impaired motor skills, slower response time, limb numbness, and impaired memory.	[181]
12	Ni	A range of respiratory conditions like asthma and Chronic lung disease are associated with it; it manifests in various symptoms, such as dry cough, nasal congestion, bluish skin, chest tightness, rapid breathing, breathlessness, and dizziness; and it is associated with various detrimental health effects, including skin allergies, pulmonary illnesses like fibrosis, neural damage, kidney disorders, and pulmonary system malignancies.	[94,182–184]
13	Pb	Infants are vulnerable to damage in their central neural system, while children may exhibit conduct problems and encounter learning challenges, including difficulties with concentration and acquiring new skills; it is connected to various health implications: blood diseases like anemia, hypertension, disorders, neural system damage, kidney illnesses, and cognitive impairment.	[94,122,162,185,186]
14	Sb	Lowering of blood sugar content and markedly increased levels of cholesterol.	[104]
15	Se	Various health effects like artery problems, loss of both nails and hair and hands and legs numbness.	[104,153]
16	Zn	It is linked to a range of health hazards, such as fatigue, increased thirst, feelings of depression, increased nervousness, stomach sickness, skin inflammation, muscular cramps, and vomiting.	[94,99,106]

6. Methods for Heavy Metal Removal

Finding effective and cost-efficient solutions to address the issue of discharges contaminated with heavy metals remains a challenge for the water treatment sector [101]. Various methods have been implemented to treat wastewater contaminated with heavy metals to safeguard human health and preserve diverse ecosystems. Some instances of such methods encompass the chemical oxidation approach [101,187], filtration technique, including membrane filtration [94,101,112], electrochemical method [99,111,188], and reverse osmosis process [187,189]. However, these methods have their drawbacks, including the significant financial burden of constructing and implementing facilities, managing operations, and using chemicals. Further drawbacks are the need for substantial power consumption, challenging working conditions, and a lower level of effectiveness in removing heavy metals, especially when the concentrations are below 100 mg L^{-1} . Moreover, these methods have been linked to producing harmful and/or potentially toxic biosolids, and the disposal of the generated waste requires more costly and environmentally damaging methods for ecosystems [99,190–192]. Different techniques for removing heavy metals, as reported in the literature, are summarized in Table 4, outlining their distinctive features and properties.

Table 4. Techniques used for removing heavy metals, along with their key aspects.

N	Technique Used	Key Benefits	Key Drawbacks	Ref.
1	Adsorption	(a) Simple process with no complexity (b) Low capital costs required (c) Efficient approach capable of removing most metals. (d) Removal ratio up to 99%	(a) Performance influenced by the adsorbent properties. (b) Significant operating expenses due to adsorbent costs. (c) No chance of adsorbent regeneration. (d) Non-selective method	[99,112,193]
2	Adsorption using magnetic materials	(a) An adsorption-based method using magnetic material (e.g., Fe ₂ O ₃). (b) Large capability for adsorption. (c) Easy metal separation. (d) High potential for reusability.	(a) A layer of polymeric substance (e.g., chitosan) is required to coat magnetic particles. (b) Particle aggregation as a result of the magnetic dipole interactions.	[194–197].
3	Biosorption	(a) Low-cost adsorbent materials (b) Excellent efficiency (c) High chance of adsorbent regeneration. (d) Low sludge volume is generated. (e) No extra nutrients for metals recovery.	(a) Adsorbents may reach saturation state early. (b) Limited usage in biological processes. (c) No change in the valence state of removed metals.	[97,198,199]
4	Chemical precipitation	(a) Uncomplicated technique with easily manageable operational variables. (b) An affordable technique (c) Capable of efficiently removing a wide range of metals.	(a) Creation of substantial sludge volumes. (b) Disposing of the sludge requires extra financial resources. (c) Ineffective settling. (d) Limited efficiency in removing trace levels of metals. (e) Performance is impacted by a lower pH extent and the presence of other ions.	[94,105,200].
5	Electrochemical treatment	(a) Selective removal of metals. (b) No need for chemical usage. (c) Obtaining pure metals is strongly achievable.	(a) Substantial capital and operating costs. (b) Significant electrical energy is needed. (c) Frequent maintenance is essential. (d) Performance is dependent on factors like the electric current and the pH.	[99,104,201]
6	Flocculation and coagulation	(a) Produced sludge settles effectively. (b) The sludge generated exhibits favorable dewatering characteristics. (c) Capable of effectively removing metals and reducing water turbidity.	(a) Costly approach with significant expenses. (b) Significant chemical quantities are utilized. (c) Amount of residue is generated. (d) Sludge disposal needs extra operational expenses.	[94,112,201].

Table 4. Cont.

N	Technique Used	Key Benefits	Key Drawbacks	Ref.
7	Flotation method	(a) More concentrated sludge is generated. (b) Effective selectivity in removing the desired metals. (c) Significant removal efficacy.	(a) Considerable installation costs (b) Significant costs associated with operation and maintenance.	[112,189,201]
8	Ion-exchange method	(a) Remarkable removal efficacy. (b) Able to achieve low concentrations in the ppb ranges. (c) Exhibiting a high degree of selectivity. (d) Very effective rate of recovery. (e) Capable of handling large quantities. (f) Rapid elimination kinetics.	(a) High installation cost, including resin expenses. (b) Limited number of metals is removed. (c) The resin recovery contributes to additional pollution. (d) Metal efficiency removal can vary depending on the type of resin used.	[104,105,202]
9	Membrane filtration	(a) The process exhibits a remarkable degree of selectivity. (b) Low pressure is required for effective operation. (c) A small spatial requirement. (d) Decreased need for chemical dependency. (e) Exceptional effectiveness with an efficiency surpassing 95%. (f) Solid waste production is very low.	(a) The process is complex. (b) Significant costs are involved in the setup, operation, and maintenance. (c) Membrane blockage problem. (d) Limited volumetric rate. (e) Large energy requirements. (f) Process effectiveness decreases with the presence of extra metals.	[94,201,203].
10	Photocatalysis	(a) Capable of effectively removing organic pollutants along with metals. (b) The method generates less intermediate compound numbers.	(a) Extended periods of reaction are required. (b) This technique has a limited scope of usage.	[99,201,204].
11	Reverse osmosis	(a) Desalination is its primary purpose of use. (b) Its potential extends to removing organic matter, minerals, and bacteria.	(a) Solid waste is generated. (b) A high level of pressure is necessary for this method. (c) The procedure involves substantial operational costs. (d) The utilization of significant power quantities. (e) Inefficient approach for removing micro-organic pollutants.	[189,201]

6.1. Biosorption Approach

Following extensive research, adsorption has emerged as a viable alternative and has demonstrated effectiveness in treating effluents polluted with metals [193,205–207]. Because of the process's inherent properties of being cost-effective and straightforward without complexity, adsorption is widely regarded as the most economical method for treating heavy metal-polluted effluents. The adsorption technique presents notable advantages, such as reduced upfront and operational costs, a simplified configuration, and decreased reliance on process control measures. In wastewater effluents, these metals are typically present in very low concentrations, around 1 milligram per liter, yet adsorption demonstrates remarkable effectiveness in removing them. Hence, adsorption has proven to be a feasible and economically viable technique for eliminating metals from wastewater [187,208]. In wastewater treatment, various traditional substances, including activated carbon and zeolites, have been used as adsorbents in effectively removing heavy metals [36,37,39,209]. Most of these adsorbents exhibit exceptional attributes such as high efficacy, good polarization, and, more importantly, large surface area, enabling them to effectively remove organic and inorganic pollutants, including metallic ions [41,42]. These adsorbents demonstrate enhanced adsorption properties when they undergo surface modification through chemical or physical treatments [42,43]. Nevertheless, the major drawback of utilizing these adsorbents is their substantial cost. Moreover, the significant costs associated with activation and the limited reusability pose major obstacles to the widespread adoption of these materials, mainly activated carbon [42,187].

In order to surpass the limitations of adsorption, biosorption has emerged as a promising method offering numerous advantages, such as cost-effectiveness, ease of operation, and remarkable efficacy, even at lower metal concentrations. The biosorption method also offers high potential for metal recovery without the need for extra nutrients. Additionally, the process is achievable within a short time, and it does not impose any adverse ecological consequences. Furthermore, bioadsorbents require minimal processing for preparation. Moreover, bioadsorbents are readily accessible in local areas, in which they can be employed to selectively target particular metals [97,199,210,211]. These substances occur naturally in the environment and are commonly derived as waste or by-products from farming activities and manufacturing processes [44,212]. Nevertheless, these substances are classified into three main groups: natural substances, agricultural residues and/or wastes, and industrial wastes [43,99,111].

6.2. Industrial Waste Adsorbents

Extensive industrial operations produce substantial quantities of solid waste materials as side products [42,211,213]. While negligible portions of these materials are being utilized, most of their amounts do not find suitable applications and are disposed of elsewhere. The fact that they are byproducts makes them readily accessible and highly affordable [111,187,213]. The presence of metal-binding groups within these wastes makes them well-suited for effective utilization as adsorbents [211]. By undergoing minor processing, the adsorption capacity of such wastes is improved [111,213]. The potential of employing a wide range of materials originating from different industries has been explored for the purpose of eliminating harmful heavy metals present in wastewater. Examples of these wastes are FA, black liquor, and red mud.

6.3. Fly Ash Material

FA is a byproduct formed during coal combustion, consisting of tiny particles carried away by flue gases [42,214,215]. FA is considered a finely textured, inorganic material with a diverse composition, consisting primarily of aluminosilicate particles. It falls within a particle size range of 1 to 100 μm and is characterized by its heterogeneity and lack of crystalline structure [216–218]. It makes up approximately 5% to 20% of the original coal and is commonly present in two forms: bottom and FA, constituting about 70% to 85% and

15% to 30%, respectively [219]. Figure 3 reveals the annual production of FA and its usage percentage by different countries.

FA contains silica (SiO_2), alumina (Al_2O_3), calcium oxide (CaO), magnesium oxide (MgO), ferric oxide (Fe_2O_3), and unburned carbon, together comprising about 90% of the total FA composition [220–222]. In addition, FA includes trace amounts of different elements such as sodium (Na), potassium (K), sulfur (S), and titanium (Ti). Although FA is known to include several essential nutrients for agricultural purposes, such as Mn, Ca, Zn, P, S, Cu, Fe, and B, it also contains several potentially harmful elements, such as Pb, Hg, Ba, As, and Cd [221].

FA can be categorized in different ways. However, there are three primary methods for FA classifications: pH level, the kind of coal from which it was formed, and its chemical makeup [222]. FA may be classified into three types based on its pH value and the Ca/S ratio. These groups are acidic ash, which has a pH between 1.2 and 7; slightly alkaline ash, with a pH ranging from 8 to 9; and highly alkaline ash, with a pH value of 11 to 13 [223]. Meanwhile, there are four distinct categories of FA: bituminous coal, sub-bituminous coal, anthracite, and lignite, depending on the coal feedstock type. According to some studies, bituminous coal FA comprises SiO_2 , Fe_2O_3 , Al_2O_3 , and Ca, along with varying carbon amounts. In contrast to FA derived from bituminous coal, FA from lignite and sub-bituminous coal has higher amounts of Mg and Ca oxides while displaying lower levels of SiO_2 , Fe_2O_3 , and carbon [224]. The chemical composition of fly ash is influenced by numerous parameters, such as the combustion techniques, the kind of coal utilized for burning, and the cooling methods implemented subsequent to combustion [225]. Thus, FA is classified into two main classes, namely class F and class C, depending on its chemical composition and in accordance with the standards established by the American Society for Testing and Materials (ASTM C618-92a). Class F refers to the kind of FA that results from bituminous coal and anthracite combustion. It is characterized by a CaO content of less than 10 wt% and an Al_2O_3 , SiO_2 , and Fe_2O_3 content above 70 wt%. On the other hand, class C FA is generated from the combustion of low-grade coal, namely sub-bituminous coal, and lignite. This particular kind of FA is characterized by a CaO content above 20% by weight, while the combined weight percentage of Al_2O_3 , SiO_2 , and Fe_2O_3 ranges from 50% to 70% [226].

FA exhibits considerable possibilities in environment-related uses and presents an intriguing substitute for conventional adsorbents in water decontamination. Nonetheless, the adsorption effectiveness of FA is greatly influenced by factors such as its source and the chemical treatment type used for enhancing its surface [213,214]. The substantial presence of SiO_2 and Al_2O_3 in fly ash renders it a favorable choice as a cost-effective adsorbent suitable for widespread usage [42]. Typically, the relatively limited adsorption capacity of untreated FA is improved by applying different treatments, including chemical and physical types [227].

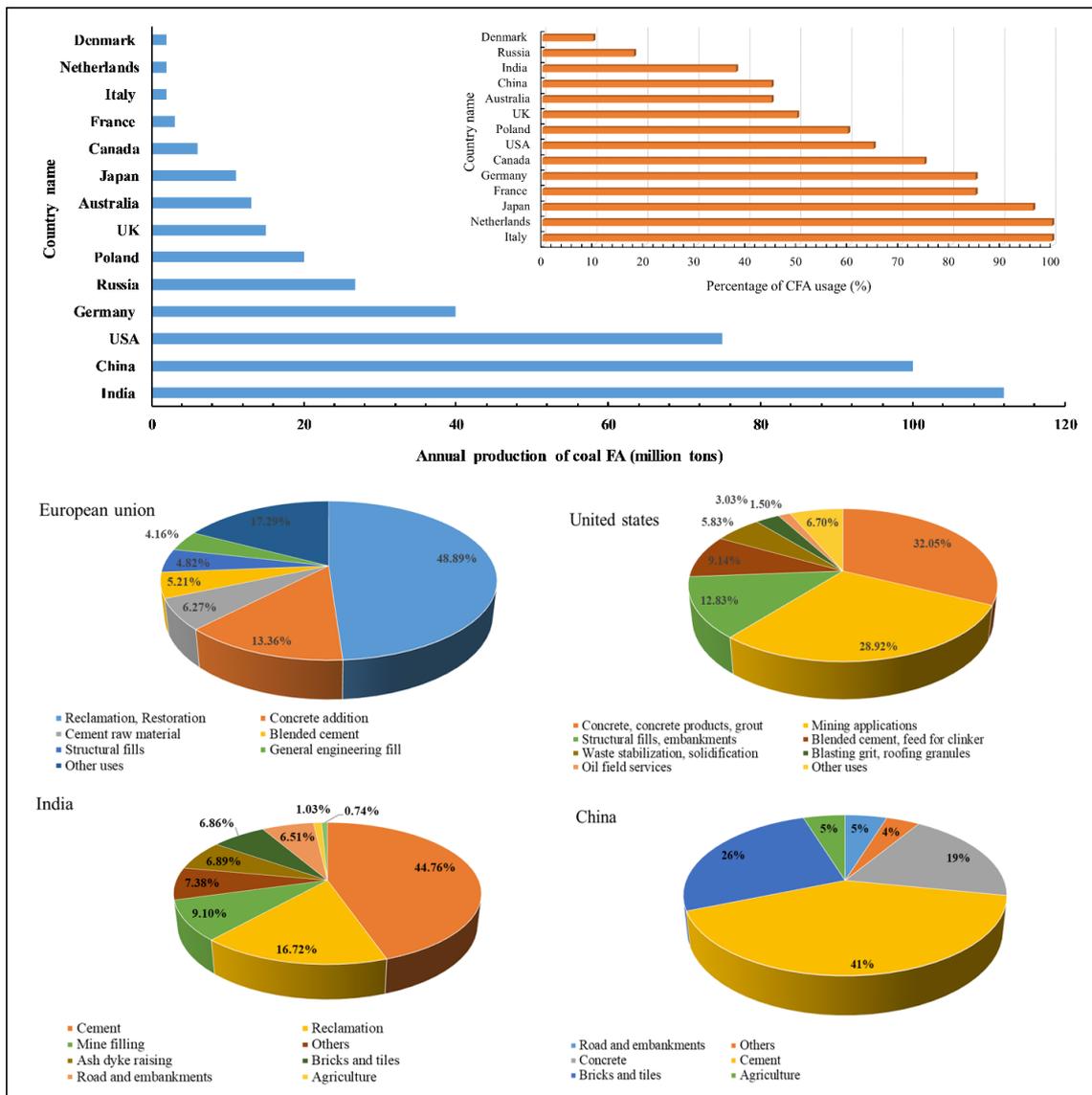


Figure 3. Annual coal FA production and its usage percent by various countries [75,228]; the included graphs are reused with the permission of Elsevier.

6.4. Use of FA for Heavy Metal Removal

6.4.1. Raw FA for Heavy Metal Removal

Using FA as an inexpensive adsorbent for eliminating metallic ions has gained widespread popularity. In terms of raw FA, Panday et al. [229] evaluated the influence of different parameters on Cu(II) removal, including metal concentrations, pH solution, adsorption temperature, and Cu(II) adsorption kinetics. The adsorption of Cu(II) onto FA has been observed to vary with the tested parameters, such as concentration and pH, indicating the dependency of these factors. It was found that the highest removal efficiency is obtained at pH 8.0, and the correlation between adsorption and pH can be elucidated by considering the surface ionization mechanism. The adsorption kinetics suggested that the diffusion mechanism controls the process, and their behaviors followed the Langmuir isotherm. Lin and Chang [230] also investigated the influence of FA properties on the decontamination of Cu(II) metal from water solutions. Their study findings demonstrated a direct linear relationship between the carbon content in FA and its specific surface area. The presence of carbon in FA played a crucial role in removing Cu(II) ions. In addition, the carbon exhibited higher specific adsorption capabilities for Cu(II), ranging between

2.2 and 2.8 mg Cu g⁻¹ carbon, whereas the mineral had lower capabilities, ranging between approximately 0.63 and 0.81 mg Cu g⁻¹ mineral.

The utilization of FA for the adsorption of Cr(VI) was examined by Grover and Narayanaswamy's [231] study. Batch experiments were carried out to assess the impact of various factors, including metal and adsorbent concentrations and pH solution, on the metallic ion removal. The highest removal efficiency was achieved at a reduced pH range and lowered Cr(VI) concentrations. The experimental data demonstrated a favorable fit for the Freundlich isotherm model. Dasmahapatra et al. [232] found that the effectiveness of FA in removing Cr(VI) is influenced by several factors, including its concentration, removal temperature, and pH. In contrast, particle size had little impact on the Cr(VI) removal. However, improved removal was achieved under a reduced pH range and at rising temperatures. Using FA, the Cr(VI) removal kinetics demonstrated a better fit to the first-order kinetics model. Meanwhile, the findings of Sharma et al.'s [233] research showed that the effectiveness of Cr(VI) removal is highly influenced by the pH, with the highest removal rate of 89.12% observed at a pH value of 2.5. It found that intraparticle diffusion plays a significant role in controlling metallic ion removal. In addition, the Cr(VI) adsorption using FA had a behavior of first-order kinetics.

The capability of coal FA to remove Hg(II) was examined by Sen and Arnab's [234] study. Different operational factors that influence adsorption were investigated, such as adsorbate and adsorbent concentrations, pH solution, and equilibrium time. Their findings revealed that the adsorption and desorption equilibrium is reached within 3 h while the pH range of 3.5–4.5 was optimal for Hg(II) removal. In addition, complete adsorption of Hg(II) was achieved at concentrations lower than 10 mg L⁻¹. Regarding kinetics, Hg(II) adsorption on coal FA was observed to follow Freundlich's isotherm. In contrast, another study [235] found that the pH range of 5.0 to 5.5 is identified as the optimal condition for Hg(II) ion removal. It was also observed that Hg(II) adsorption on FA requires 2 h to achieve an equilibrium state. Figure 4 presents Cr(VI) adsorption on FA at different pH values to achieve maximum removal.

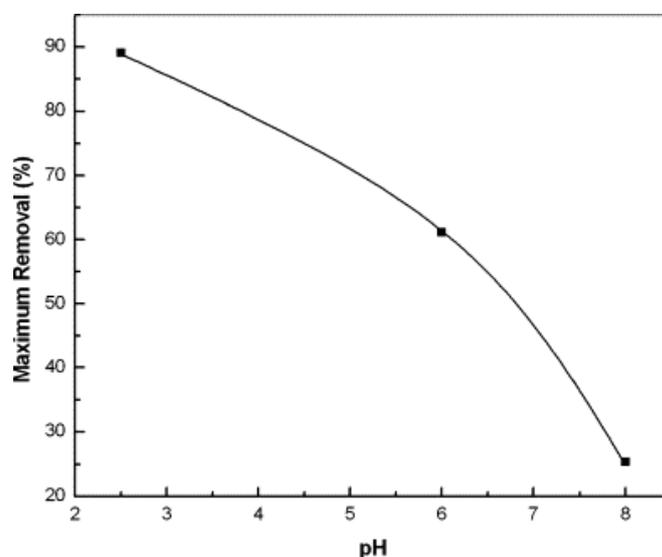


Figure 4. Optimal Cr(VI) elimination through adsorption using FA at various pH levels [233]; the figure is reused with the permission of Elsevier.

Diamadopoulos et al. [236] conducted a study on FA derived from coal-based thermal plants to assess its effectiveness in eliminating As(V) from water. The study revealed that FA has the capability to eliminate As(V). However, the effectiveness of metal ion removal varied significantly based on the pH level. As indicated by the results, the As(V) adsorption was considerably greater at a pH value of 4 compared to other pH values. In the desorption analysis, a negligible quantity of the As(V) initially adsorbed was

released into the aqueous solution. Notably, such release remained consistent regardless of the adsorbent dose, suggesting that the As(V) adsorption on the surface of FA is highly persistent and difficult to reverse. Yadava et al. [237] focused on examining the elimination of Cd(II) using FA. The Cd(II) removal mechanism demonstrated first-order kinetics, where the crucial step controlling the rate involves the transport of ions within the pores of adsorbent particles. The metal removal at various temperatures was accurately described by the Langmuir isotherm. The Cd(II) adsorption also exhibited a temperature-dependent behavior, revealing its exothermic condition. Moreover, the presence of an alkaline medium enhanced the efficacy of metallic ion removal. Weng and Huang [238] found that the Zn(II) adsorption behavior properties are predominantly governed by pH of the aqueous solution. The data indicated that removal of Zn(II) is insignificant at a pH below 4.5. However, the elimination rate exhibited a significant surge between 5.0 and 7.0 pH when the adsorbent concentration was $1 \times 10^{-6} \text{ mol g}^{-1}$. Nevertheless, the rapid rise in adsorption became limited to a pH range of 6.5 to 8.5 as the adsorbent loading reached a value of $2 \times 10^{-5} \text{ mol g}^{-1}$. The presence of Zn(OH)₂(s) precipitates was seen only at pH levels over 8.0. This emphasizes that the primary mechanism for removing zinc using ash adsorbent at pH levels below 8.0 was primarily due to an adsorption process. At pH levels greater than 8, obtaining a Zn(II) removal rate of up to 99% was possible. This may be attributed to the simultaneous occurrence of Zn(OH)₂(s) precipitation and Zn(II) adsorption processes. Subsequently, the removal rate stayed unchanged across a broad pH range. The metal ion removal was accurately described by the Langmuir isotherm. The removal also exhibited favorable behavior under reduced ionic strength, increased pH, and elevated temperature conditions. The adsorption method was found to be primarily driven by physical interactions, with the electrostatic impact playing a significant role in enhancing the procedure. Table 5 presents the physicochemical characteristics of FA obtained from different sources.

Table 5. Chemical and physical properties of FA derived from various origins.

Chemical Composition of FA		(w/w %)					
N	Major Constituents	No1 ^a	No2 ^b	No3 ^c	No4 ^d	No5 ^e	No6 ^f
1	Silica (SiO ₂)	53.32	51.0	47.42	15.14	53.50	36.06
2	Alumina (Al ₂ O ₃)	22.05	20.0	19.16	7.54	15.71	15.38
3	Iron(III) oxide (Fe ₂ O ₃)	8.97	12.5	10.89	3.30	8.81	8.28
4	Calcium oxide (CaO)	5.24	4.0	12.52	23.66	0.29	34.96
5	Magnesium oxide (MgO)	2.44	2.0	1.21	4.50	2.94	2.26
6	Potassium oxide (K ₂ O)	2.66	0.8	2.42	0.28	1.19	0.12
7	Sulfur trioxide (SO ₃)	-	-	2.82	13.22	1.11	-
8	Titanium dioxide (TiO ₂)	1.07	-	1.11	1.03	0.12	0.93
9	Sodium oxide (Na ₂ O)	0.63	0.7	0.52	0.57	0.77	-
N	Trace elements	(mg/Kg)					
10	Arsenic (As)	100.0	-	12.0	-	-	-
11	Cadmium (Cd)	-	4.0	0.2	8.0	-	1.0
12	Chromium (Cr)	100.0	71.0	327.3	298.0	454.5	70.0
13	Copper (Cu)	60.0	73.0	1.5	40.0	98.8	80.0
14	Lead (Pb)	35.0	141.0	7.6	80.0	79.0	-
15	Manganese (Mn)	800.0	956.0	378.2	219.0	790.4	10.0
16	Nickel (Ni)	55.0	73.0	297.4	119.0	1976	-
17	Zinc (Zn)	160.0	98.0	118.8	80.0	112.6	5000
Physical properties							
18	Density (g cm ⁻³)	-	0.62	-	1.05	0.88	2.51
19	Loss on ignition	1.58	7.50	2.42	2.31	3.78	4.49
20	Surface area (m ² g ⁻¹)	-	-	10.20	0.34	0.12	0.41

Remarks: (a) This data was obtained from [239]; (b) This information was obtained from [240]; (c) The data was taken from [241]; (d) FA data was gained from [242]; (e) The FA information was obtained from [242]; (f) The data on FA was obtained from [243].

Alinnor [244] examined the removal behavior of Pb(II) and Cu(II) using FA, considering various factors such as pH solution and temperature. Overall, there was an increase in the removal of Cu(II) and Pb(II) from water solutions as the pH level rose, although this increase was not consistently gradual. The adsorption of metallic ions using FA was negatively affected by higher temperatures. The removal of Pb(II) and Cu(II) using FA exhibited a fast uptake in the initial 20 min, and equilibrium was achieved in 2 h for both metallic ions. In addition, the adsorption of both metals was described by first-order kinetics. Bayat [245] assessed the effectiveness of two Turkish FA adsorbents for removing two metallic ions: Cr(VI) and Cd(II). Different FAs exhibited superior capacities towards Cd(II) ions compared to Cr(VI) ions; however, all metallic ion solutions reached equilibrium within 2 h. The proportion of lime, CaO, present in FA composition appeared to play a critical role in removing metallic ions. The Cr(VI) adsorption behavior did not fit well with the Langmuir or Freundlich isotherms, whereas the Cd(II) removal using various FA types exhibited good agreement with the Langmuir isotherm. Bayat [246] also explored the potential application of FA for the elimination of Zn(II) and Cd(II) from a water solution. Similarly, the time required to achieve equilibrium was identified as 2 h. Optimum metal removal was observed within the pH extent ranging between 7.0 and 7.5. Removing metallic ions demonstrated an upward trend as their concentrations, adsorbent amount, and adsorption temperature increased. The suitability of the Langmuir isotherm implied that Zn(II) and Cd(II) ions tend to form a single layer on the external surface of used adsorbents. The thermodynamic factors indicated that an endothermic behavior characterizes the removal method. Ayala et al. [247] evaluated the efficacy of FA in eliminating different metal ions, namely Cu(II) and Cd(II). It was found that a decrease in the pH of the solution reduces the metal removal utilizing FA adsorbent. At the same time, its removal capability showed an upward trend when the concentration of metallic ions was lowered. The removal of metallic ions was not significantly affected by the presence of elevated ionic strength or substantial levels of Ca and Cl ions. The impact of FA treatment on the metallic ions content and toxicity levels of municipal effluent was assessed by Gupta and Torres's investigation [248]. Following the treatment, the effluent registered a considerable decrease in toxicity, as well as reduced levels of the heavy metals Cu(II) and Pb(II), and inorganic ions such as PO_4^{3-} . The utilization of FA led to the adsorptive removal of Cu(II) and Pb(II), effectively reducing the presence of such hazardous heavy metals. Consequently, the effluent toxicity was significantly diminished. Sočo and Kalembkiewicz [240] evaluated the use of FA in adsorbing Cu(II) and Ni(II) ions from their water solutions. An elevation in pH level resulted in an augmentation of metal adsorption, with the peak observed at around pH 8.0 for both metallic ions. At optimal pH, the highest levels of metal elimination were observed, reaching a maximum degree of 97.7% for Ni(II) and 98.0% for Cu(II) ions. As the concentrations of Cu(II) and Ni(II) increased from 5 to 100 mg L⁻¹, the ions' adsorption exhibited contrasting trends. For Cu(II), its removal rose from 96% to 97.6%, while Ni(II) ion removal reduced from 100% to 98% over the same range. The Freundlich and second-order Langmuir models satisfactorily fitted the Ni(II) removal behavior. The elimination mechanism of Cu(II) and Ni(II) ions was mainly controlled by particle diffusion.

Bayat [242] aimed to evaluate the efficiency of two Turkish FA types as adsorbents in removing various metallic ions: Cu(II), Ni(II), and Zn(II). The findings revealed the highest level of metal elimination varied depending on the pH of the process between different metal types. An apparent variation was registered in the pH value of maximum removal for the two FA kinds. However, the solutions of various metallic ions reached equilibrium after 2 h. It was observed that the efficacy of FA as an adsorbent was positively influenced by the increasing presence of CaO in its composition. For various metals, the obtained data showed stronger conformity with the Langmuir isotherm, as evidenced by high coefficients, compared to the Freundlich model. As a part of their study, Apak et al. [249] explored the utilization of coal FA for the elimination of different metallic ions: Cd(II), Cu(II), and Pb(II) from aqueous solutions. Dynamic column tests were performed to evaluate the breakthrough amounts of the metallic ions. This allowed determination of the saturation

capabilities of the used adsorbent materials. It was obtained that the FA capabilities for adsorbing metallic ions have the following order: Cu(II) > Pb(II) > Cd(II). Such order aligns with their ability of dissolution exhibited by the respective metallic hydroxides. The feasibility of using FA as an adsorbent material for capturing different metallic ions, Mn(II), Pb(II), Cu(II), Zn(II), and Cd(II), found in the leachate of municipal waste, was examined by Mohan and Gandhimathi's study [243]. The optimal FA concentration for achieving the highest metal removal was identified as 2 g L^{-1} , resulting in removal capability values of 28%, 39%, 42%, 71%, and 74% for metallic ions Mn(II), Cu(II), Zn(II), Cd(II), and Pb(II), respectively. Examination of how the adsorption of different metal ions onto FA is affected by the contact time is shown in Figure 5.

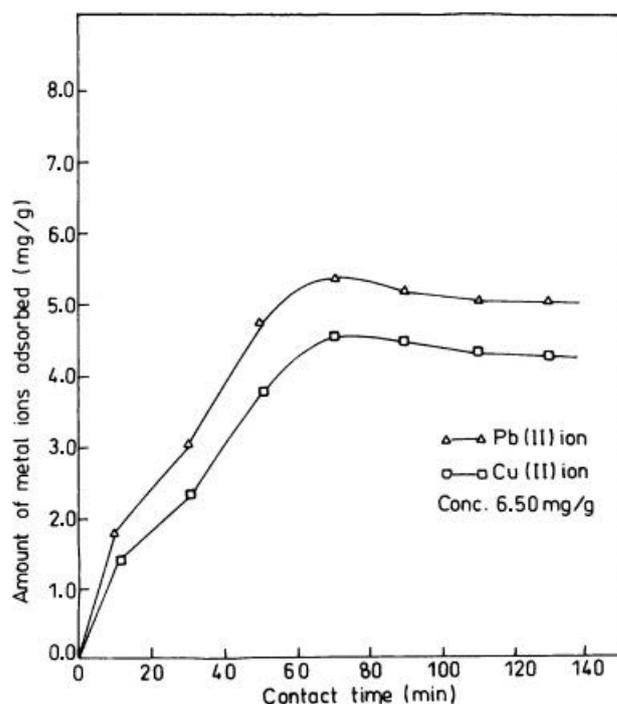


Figure 5. Influence of contact time on the adsorption of various metallic ions onto FA [244]; the figure is reused with the permission of Elsevier.

Gupta's group carried out a range of studies exploring the removal of metallic ions from aqueous solutions utilizing FA adsorbent material [250–254]. Their investigations utilized bagasse-based FA, which is a waste generated in sugar factories, to eliminate different metallic ions: Ni(II), Cu(II), Pb(II), Cr(III), Cd(II), and Zn(II). The FA demonstrated high efficiency in adsorbing Cu(II) and Zn(II), with adsorption rates between 90% and 95% employing batch and continuous runs. The adsorption process was determined to be thermodynamically favorable, with an endothermic nature, and conformed to the Langmuir and Freundlich isotherms. Approximately 90% of Cd(II) and Ni(II) ions were effectively removed within 60 min and 80 min, respectively. The findings also found that Zn(II) is completely removed at reduced ion concentrations, but its removal decreases to between 60% and 65% at high ion concentrations. The FA was capable of adsorbing Pb(II) and Cr(III) with an efficiency between 96% and 98%. Meanwhile, applying FA in continuous mode runs resulted in removing such heavy metals at 95% and 96% levels.

Regarding comparison to different adsorbents, Bhattacharya et al. [255] evaluated the elimination of Cr(VI) from water utilizing FA as an adsorbent. The adsorption capacity of FA was compared with different adsorbents like sludge and sawdust. The results indicated that sludge exhibits the highest efficacy compared to the tested types of adsorbents for metal removal. Moreover, their findings revealed that adsorption is a complicated process with two main stages. The first stage is associated with diffusion through the boundary

layer, influenced by external mass transfer impacts, while the subsequent step involves intraparticle diffusion, which plays a significant role in governing the overall rate of the adsorption process. Rao et al. [256] employed inexpensive adsorbents comprising FA and raw bagasse to eliminate two metallic ions, Cr(VI) and Ni(II), from water solutions. The obtained findings revealed that the adsorption rate relies on the experimental setup and the properties of the adsorbent material and the pollutant metallic ion. The effectiveness of adsorbents in removing Cr(VI) and Ni(II) was within the range of about 56% to 96% and 84% to 100%, respectively. Activated carbon exhibited the highest selectivity for Cr(VI) elimination, followed by raw bagasse and FA. In the case of Ni(II) elimination, activated carbon showed the highest selectivity, followed by FA and raw bagasse. The effectiveness of FA and activated carbon in the removal of Ni(II) and Zn(II) from a water solution was compared by Cetin and Pehlivan [257]. It was determined that a contact time of 1 h is necessary to achieve equilibrium in the adsorption of metallic ions using all adsorbents. The efficacy of metallic ion elimination was observed to be correlated with the pH of the solution. Furthermore, an increase in Ni(II) and Zn(II) ions reduced their adsorption on the two adsorbent types. The adsorption capacity of FA showed enhancement with an increase in the CaO content, indicating boosted efficiency as an adsorbent. The experimental results of Ni(II) and Zn(II) adsorption exhibited excellent agreement with the Langmuir model for FA and activated carbon. Rao et al. [258] employed FA and bagasse for the purpose of removing Cu(II) and Pb(II) using an adsorption approach. The effectiveness of Cu(II) and Pb(II) removal was influenced by several factors, including adsorption time, pH, adsorbent amount, particle size, and heavy metal concentration. Under optimal conditions, the capacity for removing Cu(II) ions followed the order FA > bagasse > AC, whereas, for Pb(II) ion removal, the adsorption capability was as follows: AC > bagasse > FA. Figure 6 reveals the adsorption removal behavior of some heavy metals over the FA surface compared to other adsorbents' behavior.

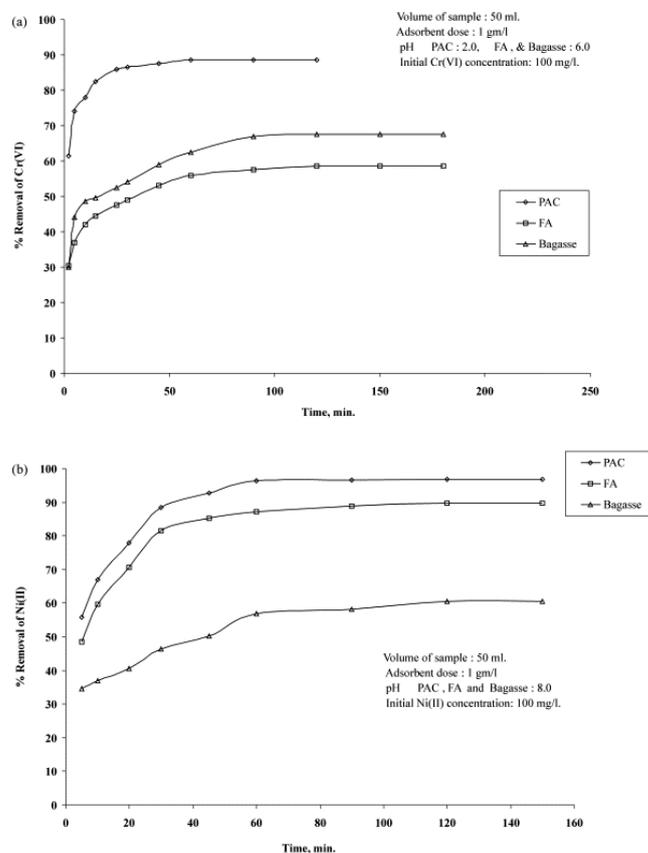


Figure 6. Behavior of metallic ion removal using FA compared to other adsorbents, (a) Cr(VI) ions and (b) Ni(II) ions [256]; the figure is reused with the permission of Elsevier.

6.4.2. Treated FA for Heavy Metal Removal

Different approaches have been utilized for FA modification, including adding different materials and chemical treatment usage to enhance its surface properties. The removal behavior of different heavy metals, including Ni(II) and Zn(II), was investigated by Banerjee et al. [259] using both raw FA and FA impregnated with Al and Fe. In comparison to raw FA, the adsorption capabilities for all metallic ions were notably higher when using impregnated FAs. The occurrence was likely attributed to forming new active sites, which are layers of Al-OH or Fe-OH. Such formation resulted from the interaction between the impregnated elements and the SiO₂ present within the FA content. It was stated that the pH-related charge usually exists at the surface edge sites, where protonation or deprotonation of the surface OH groups occurs in response to changes in pH. The binding of heavy metal cations to the impregnated FA can occur via the edge OH groups of Al and Fe present on its surface. The adsorption removal was described well by the Langmuir isotherm for different metallic ions. It was also found that the metal removal is characterized as an exothermic process for Ni(II) ions and an endothermic method for Zn(II) ions. In a similar study, the group [260] used the same adsorbents, raw FA, FA-Al, and FA-Fe, to examine the possibility of the removal of two metallic ions: Cr(VI) and Hg(II). The adsorption capability of impregnated FA for both metallic ions was identified to surpass the FA capacity. It was stated that adsorbents have the ability to selectively adsorb heavy metal cations when they have a surface layer of Al(OH)₃. The Al-OH groups with high affinity and changeable charge are primarily responsible for replacing the low-affinity sites located on the surface with permanent charge. This explanation was further confirmed by the observation that the levels of dissolved Hg(II) ions are elevated at acidic pH levels when FA adsorbent is subjected to treatment with Al and Fe ions. The removal efficacy was highly influenced by the metallic ion concentration, and the removal behavior conformed with the Langmuir isotherm. For Cr(VI) removal, the capacities of FA, FA-Al, and FA-Fe adsorbents were recorded as 1.38, 1.82, and 1.67 mg g⁻¹, respectively. Similarly, Hg(II) removal capabilities were determined as 11.0, 12.5, and 13.4 mg g⁻¹ for FA, FA-Al, and FA-Fe, respectively. Ricou et al. [261,262] investigated the efficacy of FA and an FA and lime mixture in removing heavy metals: Cd(II), Cu(II), Ni(II), Pb(II), and Zn(II). Their research found that the sequence of adsorbent effectiveness in removing the metal ions was determined as Pb(II) > Cu(II) > Ni(II) > Zn(II) > Cd(II). In addition, it was suggested that the presence of calcium silicate hydrates due to pozzolanic activity was accountable for the increase in removal efficiency and the decrease in desorption simultaneously. Weng and Huang [263] explored a method for treating industrial wastewater containing metallic ions. The method involved the utilization of FA adsorption followed by cement fixation of the adsorbent containing the captured metals. The study demonstrated that the FA exhibits capabilities of Cd(II) and Zn(II) ion removal with values of 0.05 and 0.27 mg g⁻¹, respectively. The metal-laden FA, with a metal content of 10%, was subjected to leaching tests, revealing metallic ion level amounts that fell below the permissible limits established for drinking water. Li et al. [264] synthesized a high iron oxide FA adsorbent (HIOFAA) and examined it in removing As(V) metallic ions from aqueous solutions. Through the HIOFAA synthesis, the original iron content within the FA underwent reorganization and was subsequently deposited on the HIOFAA surface via mechanisms of dissolution and precipitation. Due to its surface modification, the modified adsorbent exhibited a highly porous framework, registering a 140 m² g⁻¹ surface area, which is considered higher than the original FA area by more than 20 times. The obtained data had an excellent agreement with the Langmuir isotherm, and the capacity for As(V) adsorption was determined to be 19.5 mg g⁻¹. Scanning electron microscopy (SEM) images of a raw FA surface are presented in Figure 7.

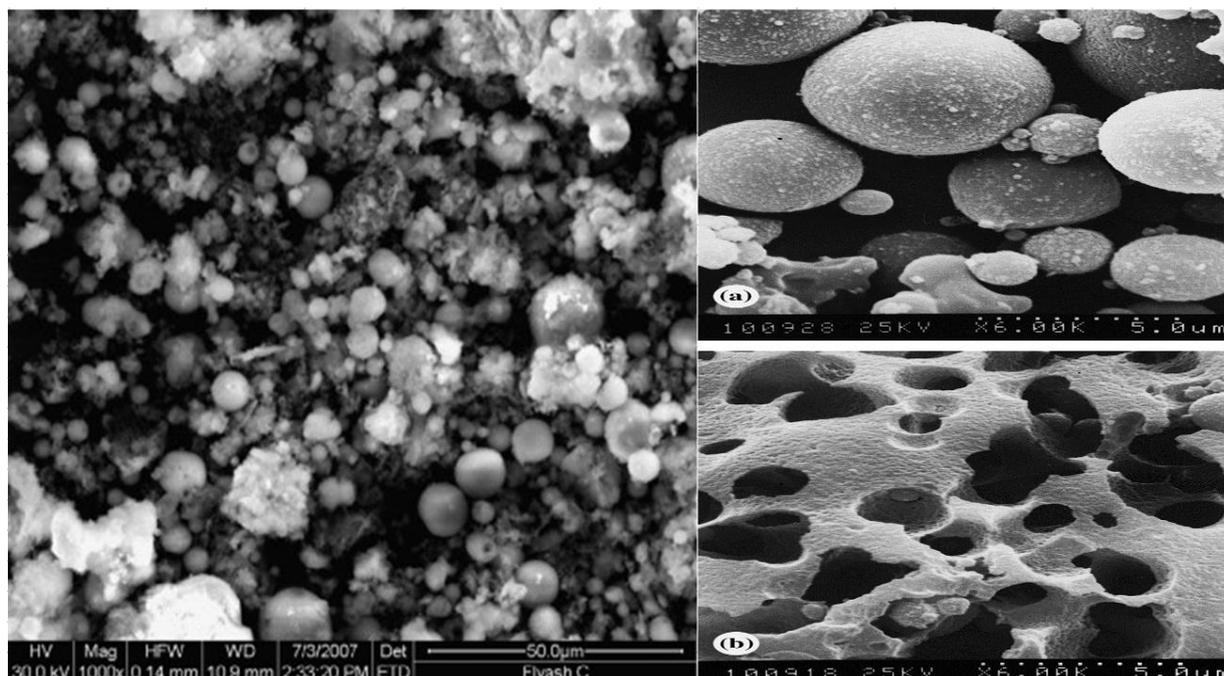


Figure 7. SEM micrographs of a raw FA surface. **Left:** surface morphology [243], **right:** texture components, (a) glass beads and (b) carbon [203]; the figures are reused with the permission of Elsevier.

Visa and Duta [265] mixed FA with TiO_2 using a hydrothermal method, and the synthesized FA- TiO_2 material was then utilized in the simultaneous elimination of metallic ions Cu(II) and Cd(II) and surfactants. The FA- TiO_2 showed remarkable effectiveness in adsorbing metallic ions, while the thin TiO_2 coverage displayed good efficiency in degrading surfactants through photocatalysis. Metallic ions and surfactants were adsorbed simultaneously from their aqueous solutions. A desirable adsorption capacity and rapid adsorption were primarily driven by the electrostatic attractions to contaminants by the synthesized adsorbent. FA- TiO_2 proved highly effective in simultaneously removing metallic ions and surfactants, ensuring that the treated water meets the required effluent guidelines. Shyam et al. [266] combined FA with CaCO_3 at two different ratios. The resulting mixtures were treated with phosphoric acid at 220°C , resulting in the formation of two substrates: FA-1:10 and FA-1:15. The formed substrates were then evaluated for their effectiveness in removing various metallic ions: Ni(II) , Pb(II) , and Cr(VI) . Substantial capabilities for removing metals were demonstrated using both adsorbents. The adsorption removal for the two substrates had the following sequence: $\text{Pb(II)} > \text{Ni(II)} > \text{Cr(VI)}$. For single adsorption, the experimental data for Cr(VI) and Ni(II) using FA-1:10 adsorbent showed good agreement with the Temkin isotherm. In contrast, the Pb(II) data on the same adsorbent conformed well to the Freundlich model. Regarding the binary adsorption, the Pb(II) and Ni(II) data on the FA-1:15 adsorbent was determined to follow the Freundlich isotherm as the most suitable model. Meanwhile, the adsorption behavior of Pb(II) and Ni(II) ions on FA-1:10 were well described by the Temkin and Freundlich models, respectively. Joshi et al. [267] synthesized $\text{Ag-Fe}_3\text{O}_4/\text{FA}$ material by depositing Ag and Fe_3O_4 simultaneously on the FA surface employing a simple hydrothermal method. The composite's capability to adsorb Pb(II) ions was evaluated by conducting a sequence of batch experiments. The findings revealed that the composite material exhibits enhanced efficacy in capturing Pb(II) ions compared to FA adsorbent. The adsorption data displayed excellent agreement with the Langmuir model, as indicated by a high regression value, suggesting a strong fit with the model. The composite registered an adsorption capability of about 527 mg g^{-1} for Pb(II) ions compared to 417 mg g^{-1} for FA particles. In addition, the Pb(II) removal had a strong conformity with the pseudo-second-order kinetics equation. Adamczuk and Kołodyńska [268] assessed the

efficacy of chitosan-coated FA as a potential adsorbent for removing different metallic ions: As(V), Cu(II), Cr(III), Cr(VI), and Zn(II). Among the studied metal ions, Zn(II) exhibited the highest overall removal rate, followed by Cr(VI) > Cu(II) > Cr(VI) > As(V) > Cr(III) in descending order of effectiveness. The Freundlich model provided a more satisfactory fit for the adsorption data of all metallic ions than the Langmuir isotherm due to obtaining high regression values. The adsorption kinetic of metallic ions followed the pseudo-second-order model. The adsorption capabilities registered values of about 55.5, 36.2, 28.7, and 19.1 mg g⁻¹ for the ions of Zn(II), Cr(III,VI), Cu(II), and As(V), respectively. The obtained thermodynamic data revealed that the adsorption process is spontaneous and endothermic. The adsorption capacities decreased as the temperature was raised. According to BET tests, the surface area of FA significantly increased from about 25.7 to 48.6 m² g⁻¹ when FA was modified with two different nanoparticles. Such behavior was consistent with the pore volume, which was drastically increased to reach a value of 0.26 cm³ g⁻¹ for the modified FA compared to its original value of about 0.07 cm³ g⁻¹ for raw FA. Incorporating tiny small nanoparticles with a large surface area onto the FA particles likely enhanced the overall surface area [267]. This was supported by the variance of the pore size distribution for the modified FA, which was completely different from raw FA. The surface area tests, including adsorption–desorption isotherms and pore size distribution, for FA and modified FA with different particles, are displayed in Figure 8.

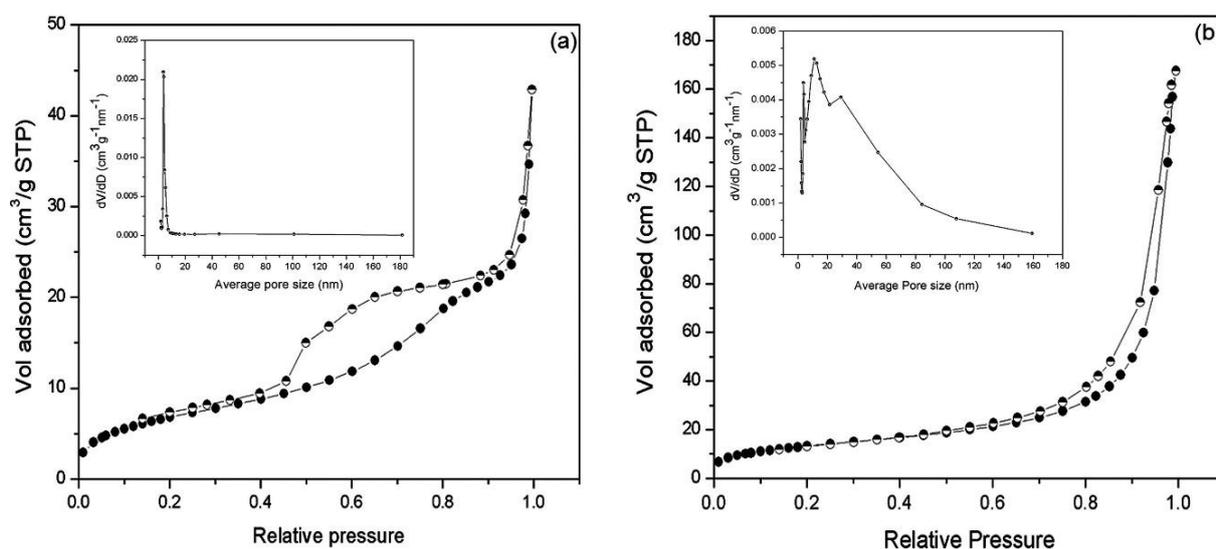


Figure 8. BET surface area tests for (a) FA and (b) modified FA with Ag-Fe₃O₄ particles [267]; the figures are reused with the permission of Elsevier.

Using the molten-salt technique, Qiu and Zheng [269] successfully produced a zeolite resembling cancrinite from an FA type. The resulting product, zeolite-FA, was utilized as an adsorbent to remove As(V). Zeolite-FA exhibited superior metal removal capability with a value of 5.1 mg g⁻¹ compared to other adsorbents: activated carbon, silica gel, a zeolite NaY type, and a zeolite 5A type, with capacities of 4.0, 0.46, 1.4, and 4.1 mg g⁻¹, respectively. Zeolite-FA's ability to adsorb As(V) more effectively than the other zeolite types used was explained by the presence of a lower ratio of Si/Al and having a secondary microstructure with porous characteristics. Nevertheless, it was observed that zeolites, due to their tiny pore structures, demonstrated reduced metal removal capabilities compared to activated alumina, which had a value of 16.6 mg g⁻¹. Following undergoing a wet impregnation with alumina, zeolite-FA experienced a considerable improvement in its removal capability. The modified zeolite-FA exhibited an impressive metal elimination capacity with a value of 34.5 mg g⁻¹, twice the value registered by activated alumina use. Zeolite X, derived from coal FA, was employed as an adsorbent for the elimination of different metallic ions: Pb(II), Cu(II), and Cd(II) [270]. The time needed to reach equilibrium

was prolonged for high heavy metal concentrations and reduced adsorbent amounts; however, in all cases, equilibrium was achieved within a maximum duration of 120 min. The pseudo-second-order model proved to be suitable for describing the kinetic behavior of different metallic ions' removal. With low metallic ions and high adsorbent concentrations, external mass transfer predominantly limited Pb(II) adsorption. In contrast, intraparticle diffusion became more prominent in governing metallic ion adsorption at high metal concentrations and reduced adsorbent amounts. Nevertheless, the Cu(II) adsorption consistently exhibited a dominant reliance on the intraparticle diffusion across the extent of concentrations evaluated. The Cd(II) removal was governed by the external mass transfer and intraparticle diffusion steps across the entire concentration range. The sequence of adsorption capabilities was as follows: Pb(II) > Cu(II) > Cd(II). Hui et al. [271] explored the utilization of zeolite 4A mixed with byproduct materials obtained from coal FA to assess their ability to remove a mixture of metallic ions using adsorption. The obtained data was successfully matched with the pseudo-second-order kinetics equation for the adsorption of Co(II), Cr(III), Cu(II), and Zn(II) ions, indicating a strong correlation. Conversely, the pseudo-first-order kinetics formula accurately described the adsorption of Ni(II) ions. The Langmuir model provided a satisfactory fit to the findings and displayed the following order for the metallic ions studied: Cu(II) > Cr(III) > Zn(II) > Co(II) > Ni(II). The mixed adsorbent exhibited relatively good removal capabilities for Ni(II) and Co(II) ions with approximate values of 9.0 and 13.7 mg g⁻¹, respectively. At the same time, it revealed superior capacities for removing Zn(II), Cr(III), and Cu(II) with registered values of about 30.8, 41.6, and 50.5 mg g⁻¹, respectively.

Cancrinite-type zeolite, obtained by the molten-salt technique to FA, was employed to eliminate different metallic ions: Zn(II), Ni(II), Cu(II), and Pb(II) [272]. The equilibrium data of various heavy metals exhibited good agreement with Langmuir isotherms. The adsorption capacity was observed to be highest for Pb(II) ions, with a value of about 2.5 mmol g⁻¹, followed by Cu(II) and Ni(II) ions, with approximate values of 2.1 and 1.5 mmol g⁻¹, respectively. Meanwhile, the synthesized zeolite had the lowest capacity for Zn(II) ions, registering a value of about 1.2 mmol g⁻¹. The pseudo-first-order model well described the removal kinetics of all metallic ions, indicating that the adsorption was governed by diffusion. He et al. [273] produced A-type zeolite from coal FA using a sequential process that includes sintering for carbon removal and acidification for iron elimination. This was followed by the step of alkali melting activation, while the final step was hydrothermal crystallization. Using synthesized zeolite, the findings showed that Ni(II) removal reaches 94%, with an adsorption capacity of 47 mg g⁻¹ when the metallic initial concentration is 100 mg L⁻¹. Additionally, the pseudo-second-order equation described the Ni(II) removal kinetics well, while the Langmuir isotherm better evaluated its ion equilibrium adsorption. The primary mechanism governing the Ni(II) ion removal using A-type zeolite was monolayer adsorption. A two-stage approach, including a hydrothermal step, was employed to synthesize two different zeolites (A and X) using FA discussed by Chunfeng et al.'s study [274]. It was observed that zeolite A exhibits higher efficacy than zeolite X in adsorbing Cu(II) and Zn(II) ions. Consequently, the focus shifted towards examining the removal efficiency of Cu(II) and Zn(II) using zeolite A, compared to zeolite obtained from residual FA (RFA-zeolite) and a commercially available zeolite A (C-zeolite A). Efficient adsorption was registered for all tested adsorbents, with Cu(II), exhibiting higher removal capacities than Zn(II). The highest removal efficiencies were achieved for Cu(II), reaching 99.7%, 89.6%, and 99.1% for zeolite A, RFA-zeolite, and C-zeolite A, respectively. Meanwhile, the removal efficiencies for Zn(II) were slightly lower at 93.2%, 81.5%, and 96.1%, respectively. Using zeolite A, the Langmuir model provided a good fit for the adsorption data of both metallic ions. Metallic ions were removed through adsorption and ion exchange, constituting the underlying ion elimination mechanism. Figure 9 presents SEM micrographs of FA and its generated zeolite at different magnifications.

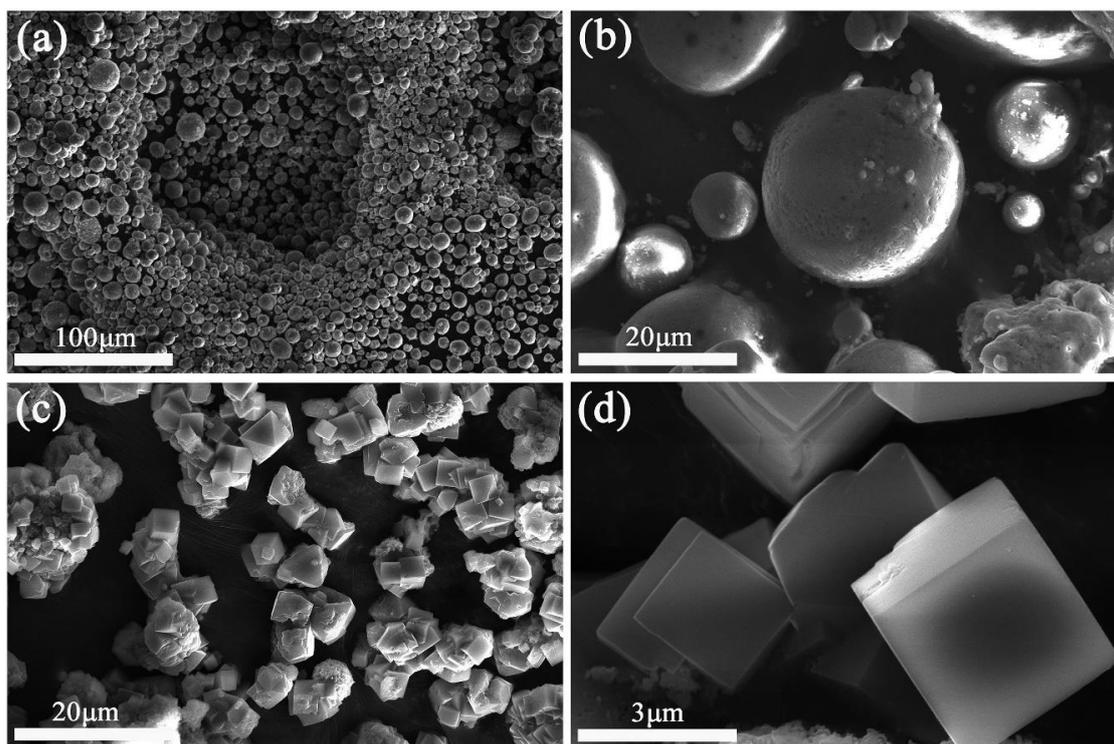


Figure 9. SEM micrographs of (a) and (b) CFA and (c) and (d) FA-generated zeolite [273]; the figures are reused with the permission of Elsevier.

Visa [275] subjected FAs to hydrothermal modification with a reduced NaOH concentration to derive zeolite materials. The zeolite substrates were then utilized for removing different metallic ions Cd(II), Cu(II), Ni(II), Pb(II), and Zn(II) from water solutions having a single metallic ion, bimetallic ions, and five metallic ions. For solutions with bimetallic ions and five metallic ions, the removal efficiency decreased for each metallic ion due to competitive adsorption occurring on comparable active surface sites of the adsorbent. The removal efficacy of different metallic ions on zeolite substrates was related to the hydrolysis constant, the adsorbed amount of metals, and the electronegativity value. According to the kinetic data, the adsorption of metals adhered to the pseudo-second-order model, suggesting a chemisorption process occurred. Kobayashi et al. [276] synthesized different zeolites by treating FA hydrothermally in an alkaline solution for 6, 12, and 24 h. The capability of the obtained zeolites, FA-zeolite-6, FA-zeolite-12, and FA-zeolite-24, was examined to adsorb Hg(II) and Pb(II) ions. It was found that FA-zeolite-24 has a higher surface area compared to other zeolites. FA-zeolite-24 exhibited a surface area that was roughly 30 times more and a pore volume that was about 98 times greater than those of untreated FA. Due to alkaline solution treatment, FA-zeolite-24 registered a surface area of $43.1 \text{ m}^2 \text{ g}^{-1}$ compared to only $1.4 \text{ m}^2 \text{ g}^{-1}$ for untreated FA. The research findings also found that the achieved surface area of FA-zeolite-24 is much higher than the surface area of synthesized zeolite obtained from FA reported by another study, with a value of only approximately $13 \text{ m}^2 \text{ g}^{-1}$ [277]. Such results revealed that alkaline solution treatment is an effective treatment technique for FA activation. The quantities of both metallic ions adsorbed on the tested adsorbents had the following sequence: FA-zeolite-24 > FA-zeolite-12 > FA-zeolite-6 > FA. FA-zeolite-24 exhibited a greater adsorption capacity for Pb(II), registering about 26 mg g^{-1} compared to Hg(II), with a value of only approximately 8 mg g^{-1} . At a high metal concentration (50 mg L^{-1}), the quantity of Hg(II) adsorbed onto the FA-zeolite-24 surface reached a value of about $22.5 \text{ m}^2 \text{ g}^{-1}$. At the same time, the Pb(II) amount was higher than $30.5 \text{ m}^2 \text{ g}^{-1}$ using the same initial concentration. According to the findings of Somerset et al.'s research [278], the quantity of Hg(II) adsorbed by a zeolite material, which was produced using the same approach, was only about $0.05 \text{ m}^2 \text{ g}^{-1}$. It should be noted

that there were some differences, although both studies used the alkaline solution treatment method. In the Kobayashi et al. [276] study, the alkaline solutions with FA were heated at 93 °C for periods ranging from 6 to 24 h periods. In contrast, the mentioned solutions were heated at 600 °C for 1–2 h in Somerset et al.'s study [278]. Similarly, prior research documented that the adsorbed amount of Pb(II) ions on natural zeolite was between 13 to 23 mg g⁻¹ [279]. The study also found a good correlation between the adsorbed amount of tested heavy metals and Na⁺ ions released from FA-zeolite-24 to the bulk solution. Such finding suggested that the quantity of heavy metal ions adsorbed is influenced by the process of ion exchange with Na⁺ ions present in FA-zeolite-24. Other research has shown patterns consistent with this investigation's findings [277,280]. Moreover, it was observed that the removal of metallic ions reached its highest efficiency at a pH of 5. Furthermore, as the adsorption temperature rose, the adsorbed quantities Pb(II) Hg(II) on FA-zeolite-24 increased, suggesting an endothermic method.

He et al. [277] subjected FA to a fusion method to synthesize zeolite, which was subsequently employed to remove various metallic ions Mn(II), Cd(II), Ni(II), Pb(II), and Cu(II). Zeolite demonstrated significantly greater removal capability than FA, and as the adsorbent amount increased, the elimination efficacy of metallic ions also increased. The elimination efficiency was noticeably impacted by the pH value and the presence of other cations whose competition capabilities were found to be as follows: Na⁺ < Mg²⁺ < Ca²⁺ < NH⁴⁺ < Al³⁺. The Langmuir isotherm provided a satisfactory fit to the adsorption data, whether in mono or multiple metallic ion solutions. The pseudo-second-order equation was suitable for the removal kinetics, except for Ni(II) and Cd(II) ions in the multiple metallic ion solutions, where the pseudo-first-order model was more appropriate. In mono metallic ion solutions, the synthesized zeolite registered the adsorption capabilities for Pb(II), Cu(II), Cd(II), Ni(II), and Mn(II) of about 65.8, 56.1, 52.1, 34.4, and 30.9 mg g⁻¹, respectively, indicating the sequence of their removal. Joseph et al. [281] examined the capability of FAU-type zeolites derived from FA for the concurrent elimination of Pb(II), Co(II), Zn(II), Cu(II), and Cd(II) ions. The synthesis method involved multiple steps: alkaline fusion, ultrapure water addition at various mass ratios, and hydrothermal treatment with different aging periods. The findings indicated that FAU zeolite could concurrently eliminate metallic ions when other ions were present. The effectiveness of FAU zeolite for removing tested metallic ions displayed the following sequence: Co(II) < Zn(II) < Cd(II) < Cu(II) < Pb(II). The adsorption of metallic ions fitted well to the Langmuir isotherm, while their removal kinetics adhered to the pseudo-second-order equation. Among the studied metals, Pb(II) registered the highest removal amount, about 110 mg g⁻¹, whereas Co(II) had the lowest amount, recording only 12 mg g⁻¹. The suitability of the intraparticle diffusion formula suggested that diffusion occurring inside the micropores played a fundamental role in governing the rate and mass transfer via boundary layers. The fusion-hydrothermal method was employed by Fan et al. [282] to produce zeolite by combining FA with municipal solid waste (MSW). The most favorable parameters for obtaining zeolite X included a NaOH/ash proportion of 1.2:1, melting temperature of 550 °C, crystallization time ranging from 6 to 10 h, and its related temperature of 90 °C. In addition, the synthesized FA-MSW zeolite exhibited a higher removal capability of Zn(II), registering a value of about 122 mg g⁻¹ compared to FA-zeolite, which removed 91.7 mg g⁻¹ Zn(II) ions. The Langmuir isotherm effectively described the removal data of Zn(II) ions than the Freundlich model. Panek et al. [283] used FA to derive two different zeolite types, Na-X zeolite and carbon zeolite (Na-X-C), which were then utilized to remove Pb(II) and Zn(II) from mono and bimetallic ion solutions. The findings revealed that the Na-X zeolite has a higher surface area of 728 m² g⁻¹ compared to the Na-X-C type, which registers a surface area of 272 m² g⁻¹. Therefore, Na-X zeolite demonstrated more effective adsorption characteristics for metallic ion removal than the Na-X-C type. Notably, the adsorption quantities for Zn(II) ions were considerably more than those for Pb(II). On the Na-X zeolite, the removal amounts were 656 and 575 mg g⁻¹ for Zn(II) and Pb(II), respectively. Meanwhile, using the Na-X-C zeolite, the corresponding values were 600 and 314 mg g⁻¹ for Zn(II) and Pb(II). The kinetics data were

most accurately described by the pseudo-second-order equation, whereas the Langmuir model was more suitable for fitting the removal isotherms. In bimetallic ion solutions, the presence of multiple ions resulted in competition for the active sites, leading to a significant decrease in their respective removed quantities. Jha et al. [284] employed FA to produce zeolitic substances suitable for the potential of polluted water purification. During the hydrothermal method of fused FA, Na-A zeolite was formed, and this could be converted into Na-X type by increasing the NaOH concentration and extending the treatment time. In terms of removal isotherms, the synthesized Na-X zeolite was studied to assess its potential for removing Pb(II), Cu(II), Cd(II), and Ni(II), in binary, ternary, and quaternary metallic ion solutions. The findings indicated that the Langmuir and Freundlich isotherms provide more precise fits than the DKR equation. With an increase in the number of ions, the matching accuracy of the Freundlich model for multiple ion solutions increased, mainly attributed to its heterogeneity property. The extended Langmuir equation effectively represented the sorption behaviors in the multiple ion solutions. However, it yielded reduced sorption values when compared to the Langmuir equation. Murukutti and Jena [285] derived different zeolites, namely zeolite-A and zeolite-X, from FA by applying an alkali fusion procedure and subsequently followed by a hydrothermal method. The zeolites' capabilities were determined by exposing them to simulated solutions with Cs^+ and Sr^{2+} ions. The BET findings showed that the FA, zeolite-A, and zeolite-X have surface area values of about 4.0, 58.3, and 164.3 $\text{m}^2 \text{g}^{-1}$, respectively. Zeolite-A and zeolite-X demonstrated elimination efficacies exceeding 90% for Sr^{2+} ions and only more than 50% for Cs^+ ions. The capabilities of zeolite-A and zeolite-X for Cs^+ ions were measured to be 54.1 and 53.1 mg g^{-1} , respectively, while their capacities for Sr^{2+} ions were 95.7 and 93.1 mg g^{-1} , respectively. Figure 10 illustrates a simplified diagram outlining the production of various zeolites from FA employing a fusion method.

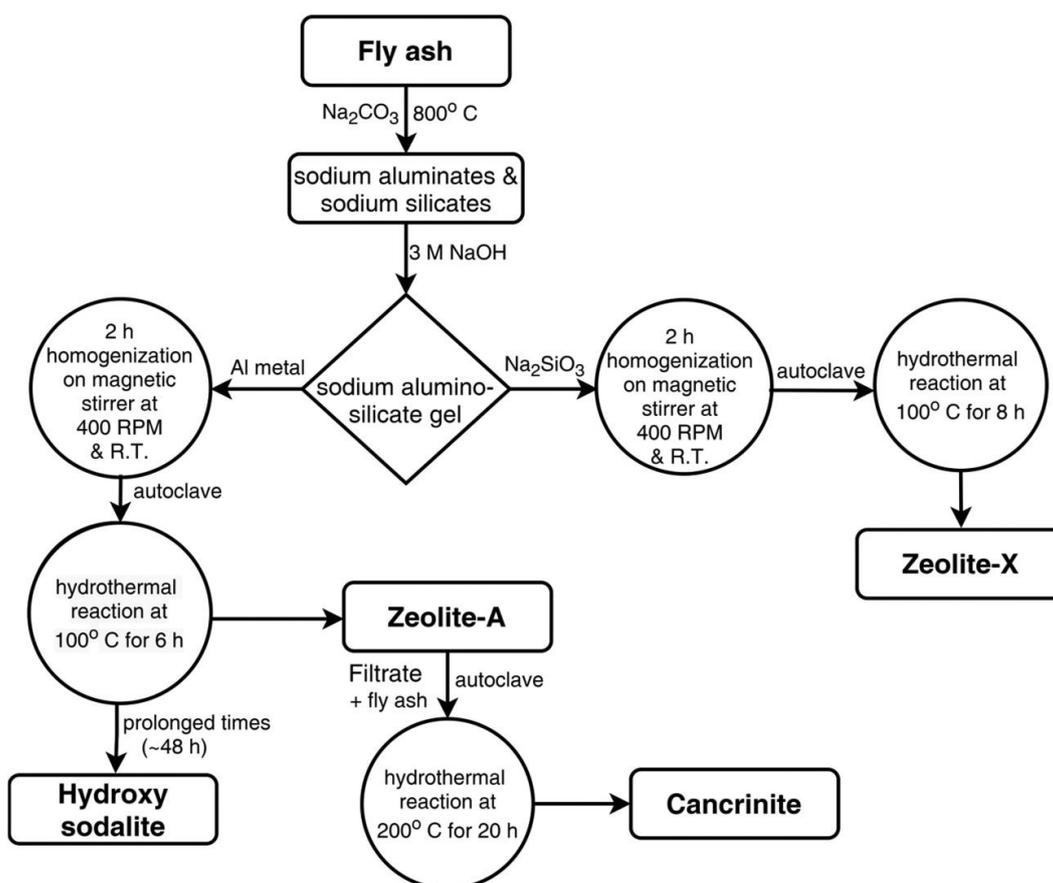


Figure 10. Schematic representation of steps for generating different zeolites using FA material via a fusion approach [285]; the figure is reused with the permission of Elsevier.

Liu et al. [286] applied a hydrothermal procedure to synthesize zeolite P using FA, and the resulting zeolite was evaluated by removing Ni(II) and Cu(II) ions. It was found that zeolite P efficiently eliminates Cu(II) and Ni(II) ions, with higher temperatures being advantageous for adsorption. The findings indicated that the second-order exchange second-order saturation equation is an excellent fit model for describing the elimination kinetics of Cu(II) ions. In contrast, the first-order empirical equation is the most appropriate model for Ni(II) kinetics removal. The Langmuir isotherm provided a good fit for the experimental data for both metallic ions. The calculated elimination capabilities for Ni(II) and Cu(II) ions were 77 and 138.1 mg g⁻¹, respectively. Bu et al. [287] discussed the potential of synthesizing NaY zeolite from coal gangue, which is rich in quartz, by employing alkaline fusion followed by a hydrothermal procedure. The most favorable factors for achieving better NaY zeolite were determined to be a Na₂O/SiO₂ ratio of 2.0, an H₂O/Na₂O ratio of 30, a crystallization temperature of 80 °C, and a period ranging between 10 and 12 h. The NaY zeolite exhibited a surface area of 759 m² g⁻¹ and a pore volume of about 0.32 cm³ g⁻¹. The resulting NaY zeolite demonstrated a remarkable Pb(II) elimination efficacy of 100%, which remained good with a value of over 63% even after undergoing five recycling times. The Langmuir isotherm and kinetic model accurately represented the Pb(II) adsorption data and its removal kinetics.

The effectiveness of two distinct FA types, silico-aluminous and sulfo-calcic, obtained from fluidized-bed processes, was examined for the removal of different metallic ions, Pb(II), Cu(II), Ni(II), Zn(II), and Hg(II), by Rio et al.'s studies [288,289]. It was found that, as the pH level rises, there is an increase in the removal capacity of metallic ions. The adsorption of heavy metals was higher when exposed to the silico-aluminous type compared to the sulfo-calcic type, with the exception of Ni(II) metal. In addition, the efficiency of Hg(II) removal was noticeably higher when employing the sulfo-calcic type. This was explained by the attachment of Hg(II) ions to the ash surface through multiple reactions between the metallic ion and different oxides in the ash. The transformation of FA into an aluminosilicate material was explored by Wang et al.'s study [290]. The resulting substance was subsequently evaluated for its effectiveness in removing Cu(II) metallic ions. It was observed that elevated temperature and a higher ratio of sodium to FA led to an increased Cu(II) adsorption efficacy. The Cu(II) removal was also influenced by the adsorbent dose and the metallic ion amount. The kinetic investigations suggested that the Cu(II) adsorption follows the second-order equation pattern. The developed adsorbent was capable of removing 92 mg g⁻¹ Cu(II) ions, which was considerably greater compared to the values of 0.1 mg g⁻¹ for raw FA and 3.5 mg g⁻¹ for natural zeolite. Pattanayak et al. [291] examined a comparison of the effectiveness of removing As(V) and As(III) using char carbon produced from FA with commercial activated carbon. The findings indicated that the As(V) removal on the char carbon is affected by the factors of pH solution, metallic ion amount, and adsorption temperature. Under optimal conditions, both char carbon and activated carbon exhibited comparable levels of As(V) removal. Regarding removal percentage, however, char carbon adsorbent demonstrated a greater ability to remove As(III) than activated carbon.

Papandreou et al. [292] molded FA into small pellets with a diameter ranging from 3 to 8 mm. The application of formed pellets was conducting experiments to effectively eliminate Cu(II) and Cd(II) metallic ions from water solutions using adsorption. The research outcomes displayed that the Langmuir isotherm model has a favorable fit for removing both metallic ions. For Cu(II) and Cd(II) ions, the adsorption capabilities registered values of about 21 mg g⁻¹ and 19 mg g⁻¹, correspondingly. In a similar study, the group [241] examined the utilization of porous pellets made from FA as an adsorbent for capturing Zn(II), Cr(III), and Pb(II) ions from their solutions. The kinetics analysis revealed that the metals' removal conforms to the pseudo-second-order model. The data obtained for all metals demonstrated a strong conformity to the Langmuir isotherm model. Among the metals studied, Pb(II) exhibited the highest level of adsorption, measuring 45.25 mg g⁻¹. This value was approximately twice as much as the capacities observed for Cr(III) (22.94 mg g⁻¹)

and Zn(II) (17.7 mg g^{-1}). Hsu et al. [293] evaluated the use of raw and modified FA to eliminate Cu(II) ions from contaminated water. Their study compared three adsorbents: raw FA, FA treated thermally at $600 \text{ }^\circ\text{C}$ (FA-600 $^\circ\text{C}$), and FA treated with NaOH (FA-NaOH). It was found that the sequence of capacities for different adsorbents is as follows: FA > FA-600 $^\circ\text{C}$ > FA-NaOH. The Cu(II) removal using raw FA and treated FA with different treatment methods was described well by second-order kinetics. Mimura et al. [294] subjected FA to a hydrothermal treatment process utilizing KOH to produce zeolite, which was then tested for eliminating radioactive cesium. It was found that the Langmuir isotherm model fits well with Cs^+ adsorption behavior on synthesized zeolite, which has a removal capability of 3.34 mmol g^{-1} . Using a similar approach, Shawabkeh et al. [295] synthesized zeolite by treating FA generated in oil shale treatment units hydrothermally using KOH. The resulting zeolite was employed to treat wastewater contaminated with Pb(II) and Cd(II) metallic ions. At a concentration of 100 mg L^{-1} for metallic ions, the zeolite registered a removal capability of about 70.6 and 95.6 mg g^{-1} for Pb(II) and Cd(II), respectively. The findings indicated that the Redlich–Peterson isotherm provided the best fit for the Pb(II) adsorption behavior, whereas the Sips isotherm model was suitable for describing Cd(II) removal. Wu et al. [296] synthesized a mesoporous material employing a hydrothermal process from FA under an alkaline environment, which was then evaluated in the elimination of Cu(II) ions. The adsorbent achieved equilibrium within approximately 20 min, and an optimal pH value of 4.4 was identified for the ions solution. The adsorption characteristics were affected by the ratio of Al to Si, and an increase in such ratio led to an enhancement in the removal capability. By fitting the obtained findings, the highest adsorption capability for Cu(II) ions was determined to be approximately 221 mg g^{-1} . The Langmuir and Freundlich isotherms accurately described the obtained data. However, the Freundlich model provided a more accurate fit to the lab data compared to the Langmuir model. A new substance was derived by subjecting FA to a gentle hydrothermal process [239]. The formed material was subsequently examined as an adsorbent for complex solutions consisting of multiple metallic ions: Pb(II), Zn(II), and Cd(II). The synthesized material effectively removed Pb(II) from multi-ion mixtures, even at various concentrations and with a short duration. However, the ion removal efficacy had the following order: Pb(II) > Zn(II) > Cd(II). Within the pH range of 5.5 to 6.6, the removal reached its maximum, indicating the optimum pH for the process. The pseudo-second-order model effectively represented the removal kinetics mechanism for the tested ions. The removal effectiveness of all metallic ions achieved using the formed adsorbent was similar to the data obtained from a commercial macro-porous adsorbent. Visa and Chelaru [297] employed hydrothermal conditions to modify FA by incorporating NaOH and a surfactant. The obtained material was subsequently evaluated for its ability to simultaneously remove methylene blue (MB) dye, and Cd(II) and Cu(II) ions. Effective removal of Cu(II) and Cd(II) was observed within 120 min, while MB removal occurred earlier, indicating satisfactory elimination efficacies for both pollutants. The significant efficiencies, exceeding 90% for MB dye, and 60% and 71% for Cd(II) and Cu(II), respectively, were mainly attributed to the distinctive morphology of the formed substrate. The pseudo-second-order model provided the most accurate description of the removal behavior for the tested pollutants. Both Langmuir and Freundlich models could model the removal behavior, proving that electrostatic attractions governed the adsorption on the highly porous material. The removal capacities of raw and treated FAs with different approaches for removing various heavy metals and their adsorption isotherms and kinetics are summarized in Table 6.

Table 6. Summary of relevant literature regarding the use of raw and treated FAs for heavy metal removal.

Metal Ion	FA Raw/Treated	pH	Capacity	Isotherm Model	Removal Kinetics	Ref.
As(III)	FA-derived char-carbon	-	89.24	No model applied	No model applied	[291]
As(V)	FA	4.0	27.78	Langmuir model Freundlich model		[236]
As(V)	FA-coated chitosan	6.0	19.1	Freundlich model	Pseudo-second-order model Intra particle diffusion model	[268]
As(V)	FA-derived cancrinite zeolite	6.0	5.1	No model applied	No model applied	[269]
As(V)	FA-derived cancrinite zeolite/modified alumina	6.0	34.5			[269]
As(V)	FA-derived char-carbon	-	34.46			[291]
As(V)	FA-high iron oxide	-	19.46	Langmuir model		[264]
Cd(II)	Bagasse FA	-	1.24	Langmuir model Freundlich model		[253]
Cd(II)	Bagasse FA	6.0	6.19	Langmuir model Freundlich model Redlich–Peterson		[298]
Cd(II)	FA	-	0.09	Freundlich model	Pseudo-second-order model	[243]
Cd(II)	FA	6.0	0.83	Langmuir model	No model applied	[246]
Cd(II)	FA	7.2	198.2	Langmuir model		[249]
Cd(II)	FA	-	0.05	No model applied		[263]
Cd(II)	FA-Afsin-Elbistan	7.0	0.29	Langmuir model		[245]
Cd(II)	FA-derived zeolite	5.0	52.12	Langmuir model	Pseudo-second-order model Pseudo-second-order model	[277]
Cd(II)	FA-derived zeolite X	-	870 ^a	Langmuir model D-R model	Vermeulen model External mass transfer model Weber–Morris model	[270]
Cd(II)	FA-pellets	-	18.98	Langmuir model	Pseudo-second-order model	[292]
Cd(II)	FA-Seyitomer	7.0	0.22	Langmuir model	No model applied	[245]
Cd(II)	FA-treated HCl	6.6	180.4	Langmuir model		[249]
Cd(II)	FA-TiO ₂	-	86.2 ^b	Langmuir model Freundlich model	Pseudo-second-order model Intra particle diffusion model	[265]
Cd(II)	FA-treated NaOH	5.6	30.21	Langmuir model	Pseudo-second-order model Intra particle diffusion model	[239]
Cd(II)	FA-washed water	6.7	195.2	Langmuir model	No model applied	[249]
Cd(II)	Oil shale FA-derived zeolite	7.0	95.6	Sips model		[295]
Co(II)	FA-derived zeolite 4A	3.0	13.72	Langmuir model	Pseudo-second-order model	[271]
Co(II)	FA-derived cancrinite zeolite	-	1242 ^a	Langmuir model	Pseudo-first-order model	[272]
Cr(III)	Bagasse FA	5.0	4.35	Langmuir model Freundlich model	No model applied	[254]
Cr(III)	FA	-	52.6	Langmuir model	Pseudo-second-order model	[299]
Cr(III,VI)	FA-coated chitosan	4.0	36.22	Freundlich model	Pseudo-second-order model Intra particle diffusion model	[268]
Cr(III)	FA-derived zeolite 4A	3.0	41.61	Langmuir model	Pseudo-second-order model	[271]
Cr(III)	FA-pellets	7.0	22.94	Langmuir model	Pseudo-second-order model	[241]
Cr(VI)	Bagasse FA	1.0	5000.0 ^a	Langmuir model Freundlich model	No model applied	[300]
Cr(VI)	FA	-	23.86	Langmuir model Freundlich model	Pseudo-second-order model Intra particle diffusion model	[255]
Cr(VI)	FA	-	1.38	Langmuir model	Pseudo-first-order model	[260]
Cr(VI)	FA/CaCO ₃ (10:1)-H ₃ PO ₄	5.0	-	Temkin model	No model applied	[266]
Cr(VI)	FA-impregnated Al	-	1.82	Langmuir model	Pseudo-first-order model	[260]

Table 6. Cont.

Metal Ion	FA Raw/Treated	pH	Capacity	Isotherm Model	Removal Kinetics	Ref.
Cr(VI)	FA-impregnated Fe	-	1.67	Langmuir model	Pseudo-first-order model	[260]
Cr(VI)	FA-wollastonite	-	2.92	Langmuir model	No model applied	[301]
Cs ⁺	FA-derived zeolite	9.5	3340 ^a	Langmuir model		[294]
Cu(II)	Bagasse FA	-	2.26	Langmuir model Freundlich model		[251]
Cu(II)	FA	6.5	1.39	Langmuir model		[229]
Cu(II)	FA	3.0	-	Freundlich model		[240]
Cu(II)	FA	-	0.05	Freundlich model	Pseudo-second-order model	[243]
Cu(II)	FA	6.0	207.3	Langmuir model	No model applied	[249]
Cu(II)	FA	6.2	0.1	No model applied Langmuir model		[290]
Cu(II)	FA	5.0	178.5	Freundlich model DKR model	Pseudo-second-order model	[293]
Cu(II)	FA	5.0	7.0	Langmuir model	No model applied	[302]
Cu(II)	FA	5.0	7.0	No model applied	Pseudo-first-order model	[303]
Cu(II)	FA-Afsin-Elbistan	6.0	1.35	Langmuir model	No model applied	[242]
Cu(II)	FA-coated chitosan	4.0	28.65	Freundlich model	Pseudo-second-order model Intra particle diffusion model	[268]
Cu(II)	FA-derived cancrinite zeolite	-	2081 ^a	Langmuir model	Pseudo-first-order model	[272]
Cu(II)	FA-derived geopolymer	6.2	90.0	No model applied	No model applied	[290]
Cu(II)	FA-derived mesoporous material	4.5	221	Freundlich model D-R model		[296]
Cu(II)	FA-derived zeolite	5.0	56.06	Langmuir model	Pseudo-second-order model	[277]
Cu(II)	FA-derived zeolite A	3.0	82.74	Langmuir model Freundlich model	No model applied	[274]
Cu(II)	FA-derived zeolite 4A	3.0	50.45	Langmuir model	Pseudo-second-order model	[271]
Cu(II)	FA-derived zeolite P	-	105.8	Langmuir model	Second-order exchange second-order saturation model. Pseudo-second-order model	[286]
Cu(II)	FA-derived zeolite X	-	1430 ^a	Langmuir model D-R model	Vermeulen model External mass transfer model Weber–Morris model	[270]
Cu(II)	FA-pellets	-	20.92	Langmuir model	Pseudo-second-order model	[292]
Cu(II)	FA-Seyitomer	6.0	1.25	Langmuir model	No model applied	[242]
Cu(II)	FA-TiO ₂	-	21.0 ^b	Langmuir model Freundlich model	Pseudo-second-order model Intra particle diffusion model	[265]
Cu(II)	FA-treated 550 °C	6.2	99.0	Langmuir model	Pseudo-second-order model	[290]
Cu(II)	FA-treated 600 °C	5.0	126.4	Langmuir model Freundlich model DKR model	Pseudo-second-order model	[293]
Cu(II)	FA-treated HCl	5.7	198.5	Langmuir model Langmuir model	No model applied	[249]
Cu(II)	FA-treated NaOH	5.0	76.7	Freundlich model DKR model	Pseudo-second-order model	[293]
Cu(II)	FA-washed water	5.8	205.8	Langmuir model	No model applied	[249]
Hg(II)	FA	-	11.0	Langmuir model	Pseudo-first-order model	[260]
Hg(II)	FA	5.0	0.73	Langmuir model Freundlich model	No model applied	[235]
Hg(II)	FA-derived zeolite-24	-	25.5	Langmuir model		[276]
Hg(II)	FA-impregnated Al	-	12.5	Langmuir model	Pseudo-first-order model	[260]
Hg(II)	FA-impregnated Fe	-	13.4	Langmuir model	Pseudo-first-order model	[260]
Mn(II)	FA	-	-	Freundlich model	Pseudo-first-order model	[243]
Mn(II)	FA-derived zeolite	5.0	30.89	Langmuir model	Pseudo-second-order model	[277]
Ni(II)	Bagasse FA	-	1.12	Langmuir model Freundlich model	No model applied	[253]

Table 6. Cont.

Metal Ion	FA Raw/Treated	pH	Capacity	Isotherm Model	Removal Kinetics	Ref.
Ni(II)	FA	8.0	4.5	Freundlich model 2nd Langmuir		[240]
Ni(II)	FA	-	0.03	Langmuir model	Pseudo-first-order model	[256]
Ni(II)	FA	4.0	0.16	Langmuir model Freundlich model	No model applied	[257]
Ni(II)	FA	6.0	14.0	Langmuir model	Pseudo-first-order model	[259]
Ni(II)	FA-Afsin-Elbistan	8.0	0.99	Langmuir model	No model applied	[242]
Ni(II)	FA/CaCO ₃ (10:1)- H ₃ PO ₄	5.0	-	Temkin model		[266]
Ni(II)	FA/CaCO ₃ (10:1)- H ₃ PO ₄	5.0	0.31–7.1 ^b	Freundlich model		[266]
Ni(II)	FA/CaCO ₃ (15:1)- H ₃ PO ₄	5.0	0.4–6.6 ^b	Freundlich model		[266]
Ni(II)	FA-derived cancrinite zeolite	-	1532 ^a	Langmuir model	Pseudo-first-order model	[272]
Ni(II)	FA-derived zeolite	5.0	34.40	Langmuir model	Pseudo-second-order model	[277]
Ni(II)	FA-derived zeolite A	-	57.74	Langmuir model	Pseudo-second-order model	[273]
Ni(II)	FA-derived zeolite 4A	3.0	8.96	Langmuir model	Pseudo-first-order model	[271]
Ni(II)	FA-derived zeolite P	-	50.29	Langmuir model	First-order empirical model	[286]
Ni(II)	FA-impregnated Fe	6.0	14.93	Langmuir model	Pseudo-first-order model	[259]
Ni(II)	FA-impregnated Al	6.0	15.75	Langmuir model	Pseudo-first-order model	[259]
Ni(II)	FA-Seyitomer	8.0	1.16	Langmuir model	No model applied	[242]
Pb(II)	Bagasse FA	6.0	2.50	Langmuir model Freundlich model		[254]
Pb(II)	FA	-	0.08	Freundlich model	Pseudo-second-order model	[243]
Pb(II)	FA	-	416.6	Langmuir model	No model applied	[267]
Pb(II)	FA	5.0	18.0	-	Pseudo-first-order model	[303]
Pb(II)	FA/Ag-Fe ₃ O ₄	-	526.5	Langmuir model	Pseudo-second-order model Intra particle diffusion model	[267]
Pb(II)	FA/CaCO ₃ (10:1)- H ₃ PO ₄	5.0	-	Freundlich model	No model applied	[266]
Pb(II)	FA/CaCO ₃ (10:1)- H ₃ PO ₄	5.0	1.4–9.1 ^b	Temkin model		[266]
Pb(II)	FA/CaCO ₃ (15:1)- H ₃ PO ₄	5.0	1.3–8.9 ^b	Freundlich model		[266]
Pb(II)	FA-derived cancrinite zeolite	-	2130 ^a	Langmuir model	Pseudo-first-order model	[272]
Pb(II)	FA-derived zeolite	5.0	65.75	Langmuir model	Pseudo-second-order model	[277]
Pb(II)	FA-derived zeolite-24	-	38.0	Langmuir model	No model applied	[276]
Pb(II)	FA-derived Na-X zeolite	5.0	676.59	Langmuir model	Pseudo-second-order model	[283]
Pb(II)	FA-derived Na-X zeolite	5.0	693.29	Langmuir model	Pseudo-second-order model	[283]
Pb(II)	FA-derived zeolite X	-	2030 ^a	Langmuir model D-R model	Pseudo-second-order model Vermeulen model External mass transfer model Weber–Morris model	[270]
Pb(II)	FA-pellets	7.0	45.25	Langmuir model	Pseudo-second-order model	[241]
Pb(II)	FA-treated NaOH	5.6	2500.0	Freundlich model	Pseudo-second-order model	[239]
Pb(II)	Oil shale FA-derived zeolite	7.0	70.58	Redlich–Peterson	No model applied	[295]
Zn(II)	Bagasse FA	-	2.34	Langmuir model Freundlich model		[251]
Zn(II)	Bagasse FA	4.0	202.0 ^a	Langmuir model Freundlich model		[252]
Zn(II)	Bagasse FA	6.0	7.03	Langmuir model Freundlich model Redlich–Peterson		[298]

Table 6. Cont.

Metal Ion	FA Raw/Treated	pH	Capacity	Isotherm Model	Removal Kinetics	Ref.
Zn(II)	FA	7.0	6.01 ^a	Langmuir model		[238]
Zn(II)	FA	-	0.03	Freundlich model	Pseudo-first-order model	[243]
Zn(II)	FA	7.0	2.78	Langmuir model	No model applied	[246]
Zn(II)	FA	4.0	0.17	Langmuir model Freundlich model		[257]
Zn(II)	FA	6.5	6.49	Langmuir model	Pseudo-first-order model	[259]
Zn(II)	FA	-	0.27	-	No model applied	[263]
Zn(II)	FA	4.0	7.84	Freundlich model		[302]
Zn(II)	FA-Afsin-Elbistan	7.0	1.16	Langmuir model		[242]
Zn(II)	FA-coated chitosan	2.0	55.52	Freundlich model	Pseudo-second-order model Intra particle diffusion model	[268]
Zn(II)	FA-derived cancrinite zeolite	-	1154 ^a	Langmuir model	Pseudo-first-order model	[272]
Zn(II)	FA-derived zeolite	-	91.72	Langmuir model	No model applied	[282]
Zn(II)	FA-derived zeolite A	3.0	47.34	Langmuir model Freundlich model		[274]
Zn(II)	FA-derived zeolite 4A	3.0	30.80	Langmuir model	Pseudo-second-order model	[271]
Zn(II)	FA-derived Na-X(C) zeolite	5.0	321.91	Langmuir model	Pseudo-second-order model	[283]
Zn(II)	FA-derived Na-X(C) zeolite	5.0	640.94	Langmuir model	Pseudo-second-order model	[283]
Zn(II)	FA-impregnated Al	6.5	7.0	Langmuir model	Pseudo-first-order model	[259]
Zn(II)	FA-impregnated Fe	6.5	7.50	Langmuir model	Pseudo-first-order model	[259]
Zn(II)	FA/MSW derived zeolite	-	121.97	Langmuir model	No model applied	[282]
Zn(II)	FA-pellets	8.0	17.7	Langmuir model	Pseudo-second-order model	[241]
Zn(II)	FA-Seyitomer	7.0	1.30	Langmuir model	No model applied	[242]
Zn(II)	FA-treated NaOH	5.6	18.87	Langmuir model	Pseudo-second-order model Intra particle diffusion model	[239]

Remarks: (a) Values were achieved in $\mu\text{mol g}^{-1}$ unit; (b) The ion adsorbed amount was obtained in multiple-ion systems.

7. Adsorption-Related Factors Analysis

Extensive research has been conducted on using FA, an industrial byproduct, as an adsorbent to remove metallic ions from wastewater solutions. While scanning the literature on FA usage in wastewater treatment applications, the main points are highlighted and summarized in the following discussion.

7.1. Operational Parameters

The findings revealed different factors affect the adsorption process, such as metal concentration, pH solution, and temperature.

7.1.1. pH Effect

pH is a crucial factor and regulatory variable in the adsorption process that is highly influenced by the pH solution. The pH of a solution has a significant role in determining the surface adsorbent charge, as well as affecting the degree of ionization and the speciation of sorbate compounds [304,305]. Within a specific pH range, the majority of metal adsorption exhibits an upward trend as pH levels rise until reaching a particular threshold, beyond which it experiences a decline with further rises in pH values. Hence, there exists an optimal pH range for adsorbing each metal onto a certain adsorbent. The influence of pH is also related to the point of zero charge (pH_{zpc}) of the adsorbent, which is the pH value at which the adsorbent is considered neutral. The adsorbent exhibits a positive surface charge when the medium has a value lower than the pH_{zpc} value. Conversely, the surface charge becomes negative when the pH exceeds the pH_{zpc} [213].

Generally, metallic ion removal is improved at a lowered pH extent. It was observed that As(V) adsorption is significantly increased at a pH value of 4 in comparison to other pH values [236]. A pH of 4.4 was determined as the optimal level for the Cu(II) ion solution. Similarly, the pH range of 3.5 to 4.5 proved optimal for eliminating Hg(II) [234]. Meanwhile, the most excellent Cr(VI) elimination rate was noted at a low pH value of 2.5 [233]. An explanation for this finding can be provided by referring to the surface charge of the FA adsorbent. According to several studies, it has been stated that FA has a low pH_{zpc} point. For instance, Weng and Huang [238] found that the pH_{zpc} of FA is 2.5, while Sahoo et al.'s study [306] found a value of 3.7 for modified FA. Similarly, the pH_{zpc} value of SiO_2 , one of FA's primary constituents, is 2 [238,306]. In contrast, other studies found that FA has a pH_{zpc} value ranging between 6 and 7 [243,307]. Likewise, the pH_{zpc} values of other components, namely Al_2O_3 and Fe_2O_3 , are 6.7 and 8.5, respectively. Therefore, it is hypothesized that the higher silica content of FA particles, compared to the content of Al_2O_3 and Fe_2O_3 , is responsible for the reduced pH_{zpc} value of FA particles [238]. This suggests that when the pH of the FA is higher than its pH_{zpc} , SiO_2 and Al_2O_3 particles present in the FA acquire a negative charge. These negative charges serve as favorable sites for the adsorption of metals and/or metal hydroxides on the FA surface [308]. As the pH climbs to a level higher than pH_{zpc} , it is reasonable to anticipate that the FA particle surfaces will become more negatively charged. This would make metals form complexes on the FA surface due to the electrostatic interaction, attractive force, between surface negative charges and cation metals, resulting in an increase in the adsorption of cationic metal ions [308,309], as shown in Equations (1) to (4). Figure 11 reveals the adsorption of Cu(II) ions at a lowered pH range with the zeta potential analysis for the used adsorbent. From the above, it can be stated that the FA content plays a vital role in the adsorption behavior of heavy metals.

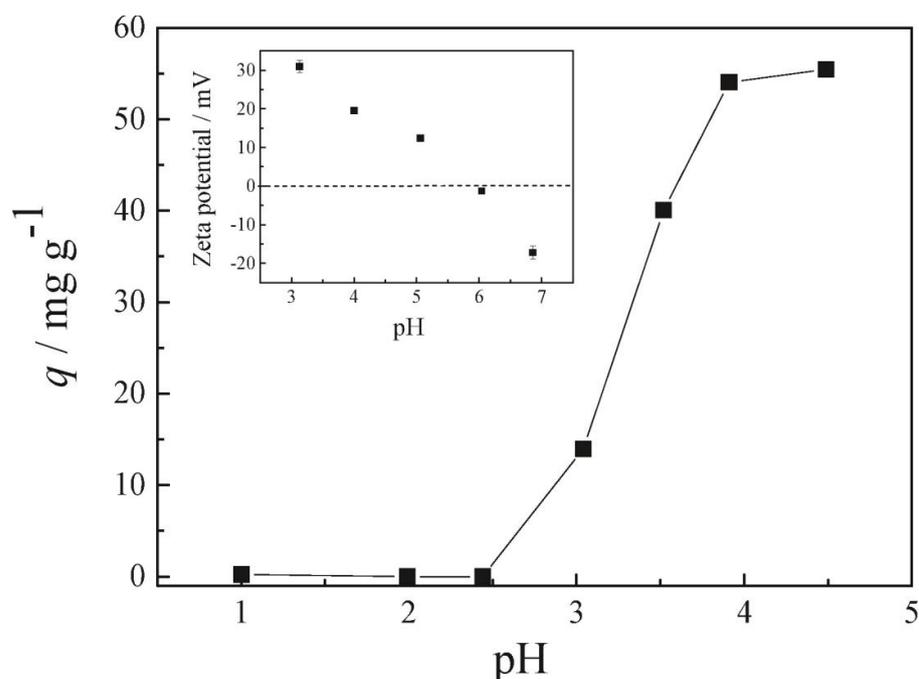
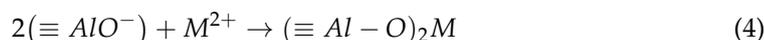
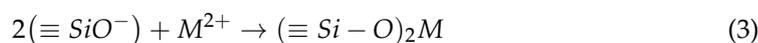
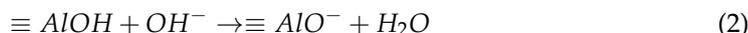
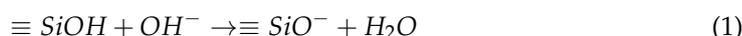


Figure 11. Adsorption behavior of Cu(II) ions on FA-zeolite adsorbent over a low pH range with the zeta potential analysis (inset) [307]; the figure is reused with the permission of Elsevier.

In contrast, removing many metallic ions exhibited favorable behavior at increased pH. For instance, increasing the pH led to increased metal adsorption, reaching its highest point at approximately pH 8.0 for Cu(II) and Ni(II) ions [240]. Similarly, the most effective removal of Zn(II) and Cd(II) metals was witnessed when the pH was maintained within the range of 7.0 to 7.5 [246]. As a result, the optimum removal of metallic ions had a broad pH range. Such behavior variation is highly dependent on the FA content and the type of heavy metal.

7.1.2. Effect of Ion Concentration

The impact of the initial metal concentrations on the adsorption capability of different waste adsorbents is significant. In general, the adsorption capability increases when the initial concentrations of the metallic ions are raised. The initial concentration of metallic ions plays a crucial role in facilitating the transfer of these metals between the aqueous bulk solution and adsorbent solid phases by overcoming various mass transfer resistances [213,214].

It was also found that the FA's ability to remove metallic ions shows an upward trend as their concentration decreased and vice versa. This behavior was obtained by many studies for different ions: Cr(VI), Cu(II), and Cd(II) [231,247]. This could be explained by the fact that the number of active sites on the FA surface is enough for absorbing all the metallic ions available in the bulk solution. Therefore, Zn(II) was completely removed at reduced ion concentrations, but its removal decreased at high concentrations [252]. However, such reduction depends on both adsorbate and metallic ion concentration.

The metallic ion removal to achieve an equilibrium state has also shown variation concerning the contact time between solutions' ions and adsorbents. The results of Sen and Arnab's [234] study indicated that the state of equilibrium for Hg(II) ions on the FA surface is achieved within 3 h. On the other hand, another study [235] found that the adsorption of Hg (II) on FA reaches an equilibrium condition after 2 h. The adsorption of Pb(II) and Cu(II) ions using FA demonstrated rapid adsorption during the first 20 min, and a state of equilibrium was reached within 2 h for both metallic ions [244]. In different studies, Bayat [242,245,246] aimed to assess the efficacy of two different Turkish FAs as adsorbents for the removal of different metallic ions: Cu(II), Ni(II), Zn(II), Cr(VI) and Cd(II). The findings revealed that the equilibrium state is achieved for the solutions containing different metallic ions after 2 h. Cetin and Pehlivan [257] conducted a comparative analysis to evaluate the efficacy of FA and activated carbon in the removal of Ni(II) and Zn(II) from an aqueous solution. In contrast, it was observed that there is a need for a contact period of 1 h to attain equilibrium in the adsorption of metallic ions utilizing all adsorbents.

7.1.3. Adsorption Temperature

The findings also demonstrated that temperature positively affects the adsorption process. Using FA, the removal of Zn(II) ions exhibited favorable performance when subjected to increased temperatures [238]. It was found that all ΔG° values have a negative sign. This observation indicated that the adsorption process occurs spontaneously, exhibiting a strong affinity of Zn(II) for FA. The free energy values exhibited a rise in negative values, from -6.86 to -7.41 kcal mol⁻¹, when the temperature escalated from 0 °C to 55 °C. This demonstrates that the adsorption becomes more advantageous at elevated temperatures. According to Bayat's study, similar behavior was registered for Cd(II) and Zn(II) ions [246]. Comparable findings have been obtained in the metal adsorption process onto different adsorbents, such as activated carbon, zeolite, Al₂O₃, TiO₂, and FA [310–313]. Moreover, as the adsorption temperature elevated, the quantities of Pb(II) and Hg(II) adsorbed onto FA-zeolite-24 escalated, implying a heat-absorbing thermodynamic mechanism [276]. In contrast, the adsorption of Pb(II) and Cu(II) was negatively affected by elevated temperatures based on the findings of Alinnor's study [244].

7.2. Effect of FA Constituents

The findings indicated a straightforward linear correlation between the carbon content within FA and its particular surface area. The existence of carbon in FA had a pivotal role in the elimination of Cu(II) ions [231]. Using two different FA types, the removal of Cu(II), Ni(II), and Zn(II) ions was assessed. It was also noted that the adsorption potential of FA is enhanced when there is a higher concentration of CaO within its content [242]. Comparable findings were obtained in removing Ni(II), Zn(II), Cr(VI), and Cd(II) ions utilizing various FA kinds. The removal capability of FA was boosted as the CaO content increased, suggesting improved efficacy for the used adsorbent [245,257]. In their study, Li et al. [264] synthesized an adsorbent rich in iron oxide content using FA. The resulting adsorbent, HIOFAA, was then evaluated for its ability to remove As(V) ions. The iron content originally present in the FA underwent restructuring and was later precipitated onto the surface of HIOFAA through dissolution and precipitation mechanisms. Because of the alteration, the adsorbent displayed an exceptionally porous structure, achieving a surface area of $140 \text{ m}^2 \text{ g}^{-1}$, which surpasses the original FA area by over twenty-fold. Using HIOFAA, the removal capacity for As(V) reached 19.5 mg g^{-1} . Wu et al. [296] employed a hydrothermal technique to synthesize a mesoporous substance utilizing FA in an alkaline medium. The obtained material was subsequently examined for its effectiveness in removing Cu(II) ions. The findings showed high removal capability is recorded for adsorbing Cu(II) ions using the synthesized material.

7.3. Effect of Materials Addition

In the study by Shyam et al. [266], FA was blended with CaCO_3 in two proportions. These resultant mixtures underwent treatment with phosphoric acid at $220 \text{ }^\circ\text{C}$, generating two adsorbents: FA-1:10 and FA-1:15. The formed adsorbents' effectiveness was then assessed in their ability to eliminate different ions: Ni(II), Pb(II), and Cr(VI). The adsorbents exhibited significant proficiency in removing these metals, with the order of removal efficiency being $\text{Pb(II)} > \text{Ni(II)} > \text{Cr(VI)}$. Joshi et al. [267] utilized a basic hydrothermal approach to synthesize a $\text{Ag-Fe}_3\text{O}_4/\text{FA}$ substance by depositing Ag particles and Fe_3O_4 oxide onto the FA surface. The results indicated that the synthesized substance removes Pb(II) ions more effectively than the unmodified FA. Fan et al. [282] utilized a fusion-hydrothermal technique to obtain zeolite through the combination of FA and MSW. The resulting zeolite displayed a superior potential for removing Zn(II) ions. Adamczuk and Kołodyńska [268] evaluated the effectiveness of FA coated with chitosan as a possible adsorbent for the elimination of various heavy metals, including Cr(III), Cr(VI), Zn(II), Cu(II), and As(V). The modified adsorbent demonstrated high adsorption capabilities for all the tested ions.

7.4. Adsorption Isotherms

Adsorption isotherms and kinetics are often used in the analysis of adsorption processes, as well as in the investigation of their mechanisms and performance. Adsorption isotherms provide valuable insights into adsorption processes and surface characteristics of adsorbents and establish a correlation between adsorbate materials and adsorbents [82]. To investigate the underlying processes of sorption, several models have been used. However, the Langmuir and Freundlich models are often reported as the most extensively used isotherm models in the existing body of literature [213]. The equation formulas of different isotherm models are presented in Table 7.

Table 7. Formulas of different isotherm models that are available in the relevant literature [314].

N	Isotherm Model Name	Model Formula
1	Dubinin–Kaganer–Radushkevich isotherm model	$Q_e = Q_m e^{-k\epsilon^2}$
2	Freundlich isotherm model	$Q_e = K_F C_e^{\frac{1}{n}}$
3	Henry isotherm model	$Q_e = K_H C_e$
4	Langmuir isotherm model	$Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e}$
5	Redlich–Peterson isotherm model	$Q_e = \frac{K_R C_e}{1 + \alpha_R C_e^\beta}$
6	Sips isotherm model	$Q_e = \frac{Q_m \alpha_S C_e^{\frac{1}{n}}}{1 + \alpha_S C_e^\beta}$
7	Tempkin isotherm model	$Q_e = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln C_e$

Remarks: Q_e represents the equilibrium adsorption capacity (mg g^{-1}); Q_m is the maximum adsorption capacity (mg g^{-1}); C_e is the equilibrium concentration of adsorbate (mg L^{-1}); K refers to the model constant whose subscript indicates the isotherm name; ($\frac{1}{n}$) (Freundlich model) represents the sorption intensity, where (n) is a constant; β (RP model) refers to the heterogeneity factor; (ϵ) (DKR model) indicates the Polanyi potential, which is related to the equilibrium concentration; (k) (DKR model) refers to a constant that is associated with the energy of adsorption; and (α_S) and (β) (Sips model) are constants.

The Langmuir isotherm is applicable when it comes to adsorption on entirely homogeneous surfaces, where there is almost no interaction between the adsorbent surface and adsorbed particles. In addition, the model considers forming a single layer of molecules adsorbed on the adsorbent surface. In contrast, the Freundlich model is applicable to the adsorption of multiple layers of adsorbed molecules on adsorbents with heterogeneous surfaces. Meanwhile, the Redlich–Peterson model characterizes the adsorption behavior of molecules on non-uniform surfaces since it includes the heterogeneity parameter (β) in its formula, which ranges from 0 to 1. The model equation may be simplified to the Langmuir model when the value of (β) reaches 1. Moreover, the Tempkin model considers the impact of various indirect interactions between the adsorbed material and adsorbent on the adsorption isotherm. The model proposes that the adsorption heat of all adsorbed molecules on the surface would fall in a linear manner as the coverage increased due to these interactions [80].

The majority of studies revealed that the removal of heavy metals follows the Langmuir isotherm. Removing Zn(II) ions fitted well to the Langmuir isotherm [238]. This outcome was confirmed by many studies. For example, using two different FA types, Bayat [242,246] found that the experimental data shows substantial conformity with the Langmuir isotherm compared to the Freundlich model. With the application of bagasse FA, the findings of Gupta’s group found the Zn(II) ion behavior has the same conformity with the Langmuir isotherm, and such an outcome was emphasized by two different studies [251,252].

Similar behavior was registered for different metallic ions: Cd(II) [237,245,246,253], Ni(II) [242,255], and Cu(II) [229,242]. The applicability of the Langmuir isotherm suggests that the adsorbed ions tend to create a monolayer on the outer surface of the utilized FA [246]. Interestingly, the FA surface modification through treatment and materials addition via impregnation did not affect the adsorption isotherm behavior of metallic ions. It found that the removal of Cr(VI) and Hg(II) using raw FA and FA impregnated with Al and Fe followed the Langmuir isotherm [260]. Similarly, the synthesized Ag-Fe₃O₄/FA demonstrated heightened effectiveness in capturing Pb(II) ions compared to the FA adsorbent. The obtained data exhibited strong agreement with the Langmuir model, evident from a high regression coefficient, implying a substantial correspondence with the model [267]. Additionally, cancrinite-type zeolite, synthesized using the molten-salt method with FA as a precursor, was utilized for the removal of various metal ions, including Zn(II), Ni(II), Cu(II), and Pb(II). The obtained data for these different heavy metals demonstrated a satisfactory fit with the Langmuir isotherm model [272]. In contrast, other studies found that Cr(VI) and Hg(II) adsorption on the FA surface follows the Freundlich

isotherm [231,234]. In terms of modified FA, Adamczuk and Kołodyńska [268] evaluated the efficiency of chitosan-coated FA as a potential adsorbent for the removal of different metallic ions, namely As(V), Cu(II), Cr(III), Cr(VI), and Zn(II). The findings for all these metal ions were more accurately described by the Freundlich model than the Langmuir isotherm, primarily due to the attainment of elevated regression values. Shyam et al. [266] integrated FA with CaCO₃ at two distinct ratios. The mixtures obtained were subjected to phosphoric acid treatment at a temperature of 220 °C, leading to the synthesis of two materials: FA-1:10 and FA-1:15. The materials that were generated were then assessed for their efficacy in eliminating different metallic ions, namely Ni(II), Pb(II), and Cr(VI). The results of experiments for Cr(VI) and Ni(II) employing FA-1:10 adsorbent displayed strong conformity to the Temkin isotherm in the context of single adsorption. Conversely, the findings for Pb(II) using a comparable adsorbent indicated a strong adherence to the Freundlich model. The dual adsorption of Pb(II) and Ni(II) on the FA-1:15 adsorbent was found to conform to the Freundlich isotherm, which is considered the most appropriate model for this kind of binary adsorption. The adsorption behavior of Pb(II) and Ni(II) ions on FA-1:10 was accurately characterized using the Temkin and Freundlich models, respectively. Jha et al. [284] used FA to generate zeolitic compounds effectively to purify contaminated water. Through the hydrothermal process of fused FA, the formation of Na-A zeolite occurred, which could be transformed into Na-X type by raising the NaOH concentration and prolonging the treatment duration. The prepared Na-X zeolite was examined to evaluate its capability for removing different heavy metals, Pb(II), Cu(II), Cd(II), and Ni(II), in binary-metal and multiple-metal systems. The results suggested that the Langmuir and Freundlich isotherms provide more accurate fits compared to the DKR equation. The accuracy of the Freundlich model for multiple ion solutions improved as the number of ions rose, primarily due to its heterogeneity feature. The expanded Langmuir equation accurately described the sorption behaviors in solutions containing several ions. Nevertheless, it produced lower sorption values in comparison to the Langmuir equation. Shawabkeh et al. [295] subjected FA produced in oil shale treatment units to hydrothermal treatment with KOH to synthesize zeolite. The synthesized zeolite was used to remediate wastewater polluted with Pb(II) and Cd(II) metal ions. The results demonstrated that the Redlich–Peterson isotherm yielded the most accurate representation of the adsorption behavior of Pb(II). In contrast, the Sips isotherm model was appropriate for characterizing the removal of Cd(II).

7.5. Adsorption Kinetics

The adsorption kinematics investigates several aspects, such as adsorption rates and rate-limiting steps [315,316]. Various models, such as pseudo-first-order, pseudo-second-order, and intraparticle, have been used to elucidate the distribution of solute ions on the adsorbent material surface and inside its pores [82]. The pseudo-first-order model is based on the hypothesis that the rate change of adsorbed solute ion over time is directly proportional to the difference in equilibrium adsorption capacity and the adsorbed amount. On the other hand, the pseudo-second-order model assumes that the rate-limiting phase is governed by chemisorption, which involves the exchange and/or sharing of electrons between the adsorbate solute and adsorbent material [317,318]. The equations of pseudo-first-order and pseudo-second-order kinetics models are presented in Equations (5) and (6), respectively.

$$Q_t = Q_e \left(1 - e^{-k_1 t}\right) \quad (5)$$

$$Q_t = \frac{k_2 Q_e^2 t}{1 + k_2 Q_e t} \quad (6)$$

where: Q_e and Q_t refer to the adsorption capacities at equilibrium and time t , respectively. k_1 and k_2 stand for the rate constants of the pseudo-first-order and pseudo-second-order kinetics models, respectively.

Regarding removal kinetics, the findings demonstrated that the process of removing Pb(II) exhibits a significant agreement with the pseudo-second-order equation through employing Ag-Fe₃O₄/FA adsorbent [267]. Zeolite X, obtained from coal FA, was applied as an adsorbent to remove diverse ions, including Pb(II), Cu(II), and Cd(II). The pseudo-second-order model appropriately described the kinetic characteristics of removing these ions [270]. The potential of employing a combination of zeolite 4A and residual materials sourced from FA was investigated. The collected data demonstrated a favorable agreement with the pseudo-second-order kinetics equation when it came to the adsorption of Co(II), Cr(III), Cu(II), and Zn(II) ions [271]. Similarly, using FA material, a zeolite was derived, which was then employed to effectively remove a range of metallic ions, including Mn(II), Cd(II), Ni(II), Pb(II), and Cu(II). In mono-ion solutions, the pseudo-second-order equation described the removal kinetics well [277]. Utilizing FA-based zeolite, similar studies found identical outcomes. The kinetics analysis indicated that the adsorption of Co(II), Cu(II), Cd(II), Pb(II), Ni(II) and Zn(II) adheres to the pattern described by the second-order equation [273,275,281,290]. Conversely, the kinetics of removing Cr(VI) ions exhibited a more suitable agreement with the first-order kinetics model using FA [232]. Similar behavior was registered for the adsorption kinetics of Cd(II), Pb(II), and Cu(II) ions with the use of FA [237,244]. Meanwhile, investigations into the applications of zeolites derived from FA revealed that the adsorption of Cu(II), Ni(II), Pb(II), and Zn(II) ions could be effectively described by the pseudo-first-order kinetics equation [271,272].

7.6. Adsorption Capacity

Generally, raw FA has a low removal capacity for heavy metals. Regarding Cd(II) ions, it was observed that the adsorption capacity of FA ranged between about 0.1 and 0.8 mg g⁻¹ [243,245,246,263]. Meanwhile, its removal capability for Cu(II) registered values at the extent of 0.1–1.4 mg g⁻¹ [229,242,243,290]. A comparable lowered range was registered for Zn(II) ions, with values of about 0.05–1.2 mg g⁻¹ [242,243,257,263]. In addition, values within the above ranges were recorded for the FA removal capacities of Hg(II) [235], Pb(II) [245], Ni(II) [256,257], and Cr(VI) ions [260]. Such behavior was mainly attributed to the limited surface area, which resulted in reduced FA capacity. Using FA as an adsorbent, however, relatively high adsorption capacities were achieved during the removal of Cu(II), Zn(II), and Hg(II) with values of 7.0, 7.8, and 11.0 mg g⁻¹, respectively [260,302,303]. Comparable capabilities were obtained in removing the metallic ions Ni(II), Pb(II), and Cr(VI), registering values of 14.0, 18.0, and 23.9 mg g⁻¹, respectively [255,259,303].

Different materials and approaches have been used to improve the FA surface area. Regarding materials addition, the FA modification with Al and Fe achieved capacities of about 1.8 and 1.7 mg g⁻¹ for Cr(VI) removal, respectively. Meanwhile, using FA-Al and FA-Fe had adsorption capabilities of 12.5 and 13.4 mg g⁻¹, respectively, for Hg(II) ions [260]. Adamczuk and Kołodyńska [268] coated FA with chitosan to examine the removal of different heavy metals, including As(V), Cu(II), and Zn(II). The coated FA was able to remove 19.1, 28.7, and 55.5 mg g⁻¹ of As(II), Cu(II), and Zn(II) ions, respectively. Fan et al. [282] mixed FA with MSW, employing a fusion-hydrothermal approach to generate zeolite material. The resulting FA-MSW zeolite eliminated 122 mg g⁻¹ of Zn(II) ions compared to 91.7 mg g⁻¹ using FA-zeolite. In their study, Papandreou et al. [292] shaped FA into compact pellets, which varied in diameter between 3 to 8 mm. It was observed that the FA-pellets have reasonable removal capabilities for Cu(II) and Cd(II) metallic ions, registering 21 and 19 mg g⁻¹, respectively. The same FA-pellets were evaluated in removing various metallic ions: Cr(III), Zn(II), and Pb(II). The formed pellets displayed good adsorption capacities, with values of 17.7, 22.9, and 45.3 mg g⁻¹ for Zn(II), Cr(III), and Pb(II) ions, respectively [241]. In their research, Hui et al. [271] investigated the potential usage of a combination of zeolite 4A and residual materials derived from FA. The combined adsorbent exhibited reasonably effective adsorption abilities for Ni(II) and Co(II) ions, with corresponding values of about 9.0 and 13.7 mg g⁻¹, respectively. Meanwhile, it

demonstrated excellent potential for effectively removing Zn(II), Cr(III), and Cu(II) ions, achieving recorded values of approximately 30.8, 41.6, and 50.5 mg g⁻¹, respectively.

Following different approaches, various zeolite types were generated from FA, and their capabilities were then examined in removing heavy metals. In their study, He et al. [277] employed a fusion technique to create zeolite from FA. The resulting zeolite exhibited a high ability to adsorb Mn(II), Ni(II), Cd(II), Cu(II), and Pb(II) ions, with recorded values of 30.9, 34.4, 52.1, 56.1, and 65.8 mg g⁻¹, respectively. Kobayashi et al. [276] produced various zeolites through the hydrothermal treatment of FA in an alkaline medium for different periods. FA-zeolite-24 displayed increased removal capability for Pb(II), recording around 26 mg g⁻¹, while its capacity for Hg(II) was notably lower, measuring about 8 mg g⁻¹. Liu et al. [286] employed a hydrothermal method to create zeolite P from FA, and the produced zeolite was assessed for its ability to eliminate Ni(II) and Cu(II) ions. The computed removal efficiencies for Ni(II) and Cu(II) ions were 77 and 138.1 mg g⁻¹, respectively. He et al. [273] generated A-type zeolite from FA, employing a sequential approach involving sintering to eliminate carbon content and an acidification step to eliminate iron presence. Subsequently, the process included alkaline melting activation, with the concluding phase being hydrothermal crystallization. Employing the produced zeolite, an adsorption capability of 47 mg g⁻¹ was registered for Ni(II) ions at an initial metal level of 100 mg L⁻¹. Shawabkeh et al. [295] produced zeolite through a hydrothermal treatment process using KOH on FA derived from oil shale processing units. The zeolite exhibited adsorption removal of roughly 70.6 and 95.6 mg g⁻¹ for Pb(II) and Cd(II) when tested with a concentration of 100 mg L⁻¹ for heavy metals. Bu et al. [287] explored the feasibility of producing NaY zeolite using quartz-rich coal gangue through an alkaline fusion and hydrothermal process. The surface area of the NaY zeolite was found to be 759 m² g⁻¹, which showed superior effectiveness in removing Pb(II), achieving a 100% removal rate, and maintaining a substantial efficiency of over 63% even after being recycled five times. In their study, Panek et al. [283] used FA to produce two distinct zeolite types: Na-X zeolite and Na-X-C. These zeolites were subsequently employed to eliminate Pb(II) and Zn(II) ions from solutions containing single and multiple ions. The results indicated that the Na-X zeolite exhibits a greater surface area of 728 m² g⁻¹, whereas the Na-X-C displays a surface area of 272 m² g⁻¹. With the Na-X zeolite, the removal capacities were recorded as 656 and 575 mg g⁻¹ for Zn(II) and Pb(II), respectively. In the case of the Na-X-C zeolite, the respective values were 600 and 314 mg g⁻¹ for Zn(II) and Pb(II), respectively. By employing the molten-salt approach, Qiu and Zheng [269] effectively created a zeolite that exhibited similarities to cancrinite using an FA. The zeolite-FA demonstrated enhanced ability in removing As(V) ions with a capacity of 5.1 mg g⁻¹, surpassing other adsorbents such as zeolite 5A and activated carbon, which displayed capabilities of 4.1 and 4.0 mg g⁻¹, respectively. After being impregnated with alumina, the zeolite/alumina-FA displayed a remarkable capability for As(V) at 34.5 mg g⁻¹, which was twice the amount achieved through activated alumina.

7.7. Removal Mechanism

The adsorption process comprises two primary phases. The initial phase pertains to the diffusion occurring at the boundary layer, which is impacted by external mass transfer influences. The following phase encompasses intraparticle diffusion, a crucial factor in controlling the total rate of the adsorption mechanism [255]. It was found that the primary factor influencing the removal mechanism of Cu(II), Cr(VI), Cd(II), and Ni(II) ions is particle diffusion [229,233,240]. Intraparticle diffusion has an important role that governs the speed, which entails the movement of ions through the pores of the adsorbent particles [237]. Additionally, the elimination of different heavy metals, Cu(II), Pb(II), Ni(II), and Zn(II), was evaluated using an FA-based zeolite. It was observed that diffusion plays a crucial role in governing the adsorption process of the tested ions [267]. Moreover, zeolite X, synthesized from FA, was used to effectively remove diverse heavy metals, including Cd(II), Cu(II), and Pb(II) [265]. It was found that the dominant factor constraining Pb(II) adsorption

is the external mass transfer at low levels of heavy metal ions and high adsorbent dose. On the other hand, the significance of intraparticle diffusion increased in controlling the adsorption of heavy metal ions at high metal levels and decreased adsorbent quantities. However, Cu(II) adsorption primarily depended on intraparticle diffusion across the entire range of concentrations examined. Meanwhile, the adsorption of Cd(II) was regulated by external mass transfer and intraparticle diffusion effects throughout the tested metal ion concentrations.

8. Cost Analysis

Examining the economic viability of an adsorbent is a crucial factor in the selection process, thus requiring a comparison of the costs associated with available adsorbents [44]. In this study, the price of FA was compared with different commercial adsorbents and their prices were obtained from the relevant literature. The average prices of commercial adsorbents, zeolite, activated alumina, and activated carbon were US\$ 450, US\$ 750, and US\$ 1150 per tonne, respectively [42,44]. The price of ion exchange resin per tonne was US\$ 4400, while the cost of CFA was found to be only US\$ 28 per tonne. It is essential to mention that the cost of these materials is widely varied, and they may not reflect the current prices. However, such prices are considered reasonably validated since they were reported in the relevant literature.

The cost price per kg of different adsorbents compared to CFA is plotted in Figure 12. A huge cost-price difference is observed between ion exchange resin and other adsorbents, including CFA. Thus, the price of ion exchange resin appears to be not comparable with other adsorbents due to its high cost of US\$ 4.4 kg⁻¹. As presented, a significant cost-price difference is noticeable between raw CFA and other commercial adsorbents. The cost per kg of raw CFA is about US\$ 0.03, while activated carbon costs US\$ 1.15 kg⁻¹, registering the highest price difference. Such cost difference becomes lowered for activated alumina and zeolite. As a result, replacing CFA with various commercial adsorbents is economically cost-effective.

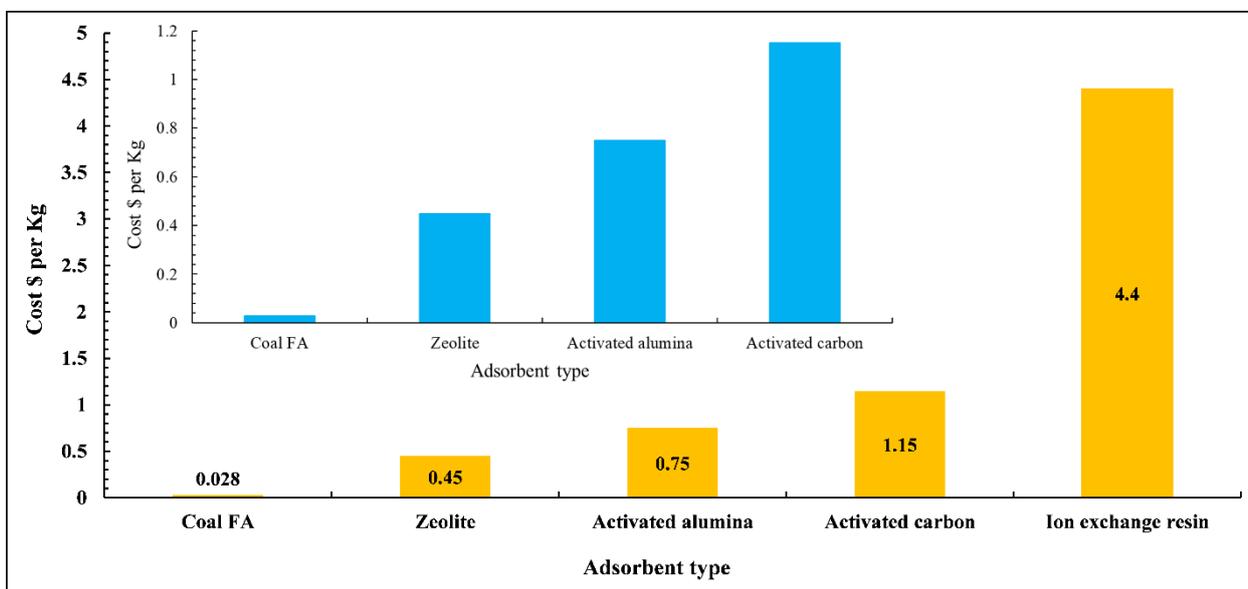


Figure 12. The cost price of raw CFA compared to other commercial adsorbents.

It is known that low-cost adsorbents like agricultural wastes require chemical and/or physical activation methods to convert them into activated carbon [50,319]. Similarly, industrial wastes like FA need such treatment methods to activate them, remove undesirable materials, and enhance their adsorption capabilities. However, the mentioned treatments would add additional expenses to the FA cost.

To achieve a fair cost analysis, the activation cost of FA was added, compared with several activated carbons, and is presented in Figure 13A,B for physical and chemical activations, respectively. The analysis consists of the price of five activated carbons with different origins, including wood, petroleum coke, carbon black, charcoal, and lignite. In terms of physical activation, the final product prices of those materials were US\$ 1.54, US\$ 1.92, US\$ 0.96, US\$ 1.72, and US\$ 1.54 per kg, respectively. Meanwhile, their final prices following chemical activations were US\$ 1.54, US\$ 5.76, US\$ 0.96, US\$ 3.84, and US\$ 4.22 per kg, respectively [320]. In addition, the activation cost of FA was chosen to be comparable to that of wood for both chemical and physical activation treatment. Therefore, the activation cost was added to obtain the final FA cost, which was then compared with the final prices of activated carbons with different origins. The analysis outcomes are presented in terms of cost savings in Figure 13A,B.

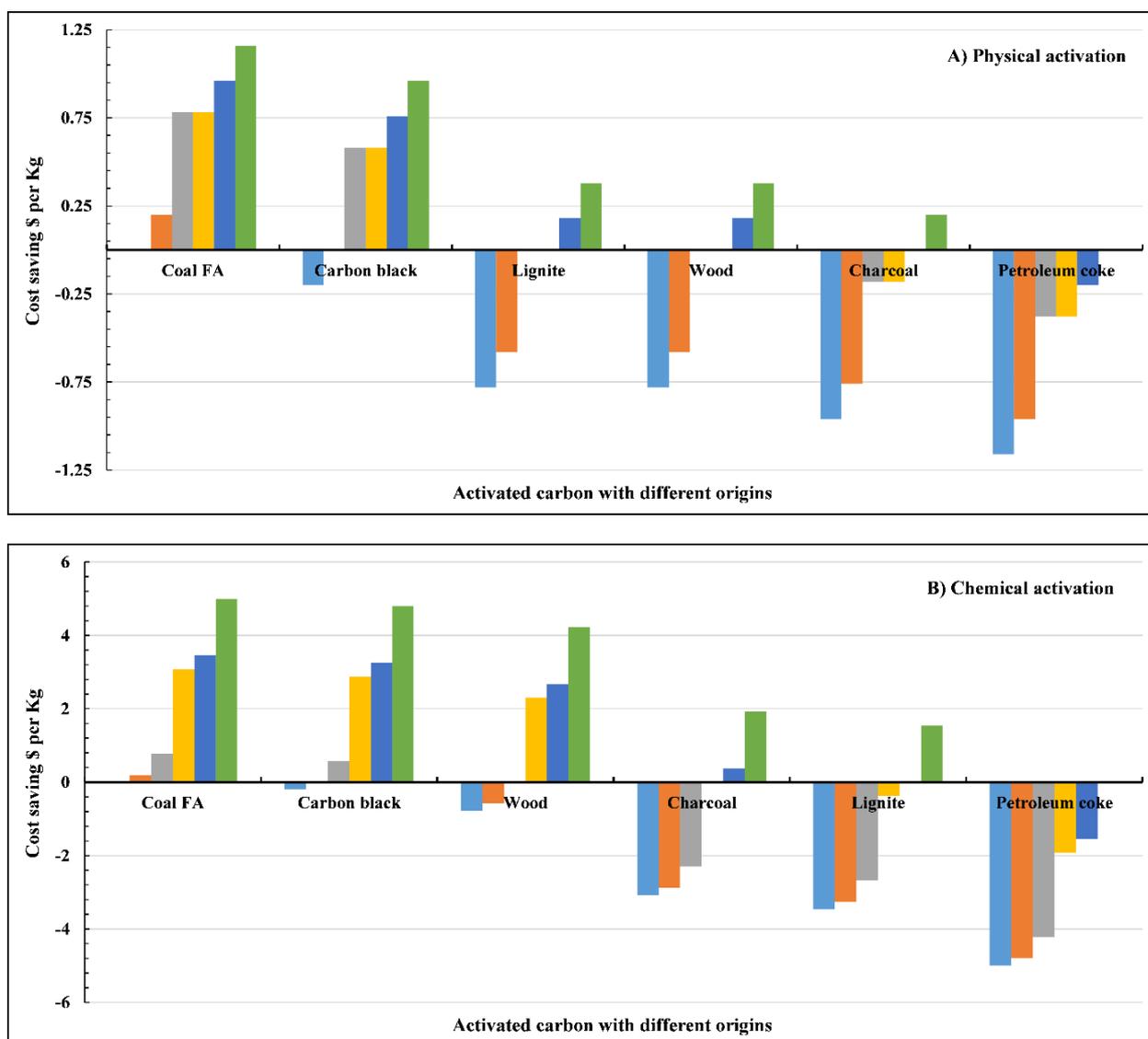


Figure 13. Cost savings of treated FA usage compared to activated carbons with different origins: (A) physical activation and (B) chemical activation.

It is observed that the cost-saving of physically activated FA usage was generally lower than that of chemically activated FA utilization. The savings ranged between US\$ 0 kg⁻¹ and US\$ 1.2 kg⁻¹ for applying physically activated FA compared with other activated carbons. Meanwhile, the savings of chemically activated FA were within the US\$ 0– US\$ 5

range. This could be due to the high cost of chemicals compared with physical methods like heat treatment. Regarding physical activation, the saving of treated FA usage was about US\$ 1.2 kg⁻¹ compared with activated carbon generated from petroleum coke, registering the highest cost-saving. In contrast, the savings of treated FA utilization were only US\$ 0.2 kg⁻¹ compared with activated carbon generated from carbon black usage. In terms of chemical activation, the savings of treated FA had a value of US\$ 5 kg⁻¹ compared to activated carbon produced from petroleum coke. Treated FA usage registered a US\$ 3.46 kg⁻¹ saving compared to the application of activated carbon obtained from lignite, as shown in Figure 13B. Meanwhile, using treated FA achieved US\$ 0.2 kg⁻¹ savings compared to employing activated carbon generated from carbon black. Thus, it is concluded that applying treated FA with both physical and/or chemical treatment is highly cost-effective and can lead to huge savings compared to commercial adsorbents.

9. FA Regeneration and Reusability

The recovery and reusability of metal-based adsorbents are assessed by regeneration and desorption research, which yields significant insights that may contribute to preserving the environment and reducing operating expenses [82]. In terms of FA regeneration, Papandreou et al. [292] shaped FA into compacted spheres measuring between 3 and 8 mm in diameter. The objective of the study was to investigate the efficacy of produced pellets in removing Cu(II) and Cd(II) metallic ions from aqueous solutions via the process of adsorption. Desorption studies were conducted to assess the ability of FA pellets containing Cu(II) and Cd(II) to release metal. FA pellets impregnated with Cu(II) and Cd(II) were subjected to drying at a temperature of 60 °C. Subsequently, 5 g of the dried FA pellets were introduced into a glass reactor containing an aqueous solution at 25 °C. Solutions with different pH values were utilized to conduct the desorption runs. The first two solutions included acidic solutions generated using acetic acid with pH values of about 3 and 5. Meanwhile, the other two solutions were deionized water and a NaOH solution with a pH of 12. The desorption findings indicated that both Cu(II) and Cd(II) were significantly released from the metal-FA pellets when exposed to acidic solutions. To prevent metal desorption, concrete blocks were created by combining cement with raw FA and then encapsulating metal-soaked pellets inside them. The efficacy of immobilizing heavy metals was assessed by subjecting concrete blocks containing encapsulated heavy metals to desorption experiments in various water solutions. The findings demonstrated that, during 60 days in an acidic environment with pH levels of about 3 and 5, Cu(II) and Cd(II) ions were not released, confirming the concrete block's exceptional ability to effectively immobilize heavy metals. Using an alkaline NaOH solution method, Soho et al. [306] improved FA adsorption capacity. FA was added to a 1M NaOH solution and then heated at a temperature of 90 °C for 24 h. The modified FA was then tested to remove various heavy metals, including Mn(II), Zn(II), Cd(II), and Ni(II). The desorption studies were conducted using the metal-modified FA obtained from the adsorption runs. Two solutions, acidic and neutral, were used to determine the modified FA's ability to release metals. The acidic solution, generated using HCl with a pH value of 2, and the deionized water solution (pH 6.5), were used for desorption experiments. In these experiments, amounts of the metal-FA adsorbent (30 g) were added to 1 L of solutions, and the suspensions were then shaken for 7 h before evaluating the metals' release. The study findings indicated that the release of metal ions under acidic conditions was much more remarkable than that in neutral conditions. Observations revealed that, under acidic conditions, a significant proportion of metals (ranging from 76% to 98%) were desorbed during the first 3 h, with the exception of Mn, which exhibited a desorption rate of 57%. Subsequently, the desorption rates slowed down. In contrast, a minimal quantity of metals, less than 5%, were desorbed from the metal-modified FA in a neutral medium, except Cd(II), which registered a released amount of less than 8.5% during the whole duration of the experiment. It was demonstrated that removing metal includes the metal cations being stably adsorbed and complexed on the reactive active sites of FA. The minimal proportions of adsorbed metal amounts released during the desorption experiments suggest that the

metal trapped in FA is chemically stable over a prolonged period. The most effective method for extracting metals from the modified FA in an acidic environment is likely due to the protonation of the FA surface, which prevents it from attracting the metal ions with positive charges and results in the protons replacing the bonded metal ions. In comparison, it was seen that Cd has a higher desorption rate in different mediums among the tested heavy metals. In Kumar et al.'s study [321], an adsorbent FA was obtained from a power generation plant. First, the FA was cleansed with a solution of HNO₃ acid. Then, it was crushed employing a mill and sifted to obtain a powder with a particle size of 45 nm. The FA was analyzed for its efficacy in removing Cd(II), Ni(II), and Cu(II) ions, both individually and in multi-metal solutions. The desorption studies were conducted using three different solutions with three different acids, H₂SO₄, HCl, and HNO₃, which were used as agents for removing the loaded metals. The metal-FA adsorbents were placed in flasks and shaken for 24 h. Subsequently, the filtrates were subjected to additional analysis to determine the portion of heavy metal ions that had been desorbed. Three separate cycles of biosorption and desorption were carried out in succession for a comparable adsorbent, with the weight loss of the adsorbent being monitored in each cycle. During the first two cycles, there was a notable reduction in weight due to the removal of soluble substances during washing. In contrast, no substantial weight loss was measured after the last cycle because the residual adsorbent could have included material resistant to dissolution. It was suggested that the corrosive properties of the used acids and the possible washing away of some surface functional groups on the adsorbent are responsible for this observed decrease in adsorption over cycles. Other studies confirmed the observation of adsorption decrease over cycles [322,323]. Among different acids used, the highest desorption efficiency was achieved with H₂SO₄ acid, which registered efficiencies of about 80% for Cu(II) ions and 72% for Ni(II) ions. Meanwhile, Cd(II) ions had a bit higher than 67% removal rate using the same acid. In addition, the desorption using HCl acid as a removal agent showed the lowest rate compared to other acids. According to the desorption investigations, it is evident that a large portion of heavy metals can be effectively removed from the FA surface in acidic mediums. This suggests that the FA adsorbents have the potential to be effectively regenerated and reused with high efficiency. The desorption of different metallic ions from an FA adsorbent under various conditions is presented in Figure 14.

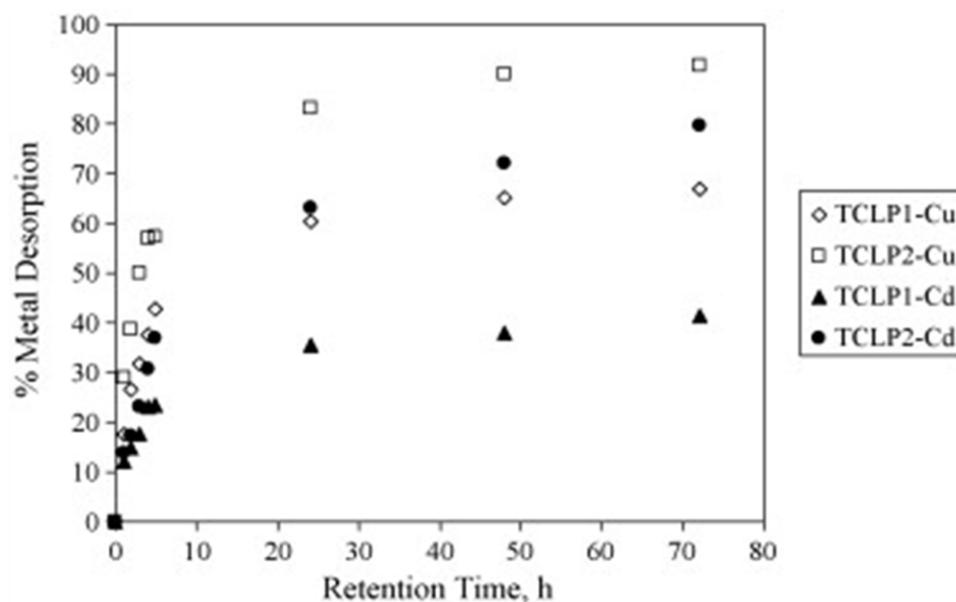


Figure 14. Desorption of various heavy metals from FA-based pellets in different mediums (TCLP refers to the U.S.EPA TCLP leaching method) [292]; the figure is reused with the permission of Elsevier.

10. Future Perspectives

Based on the related literature, the considerable potential of FA, a byproduct of coal combustion, in ecological-related implementations, is indisputable. FA is an intriguing option that may be used in lieu of typical choices that rely on a chemical and/or petrochemical basis, such as activated carbon, in the context of adsorption processes for water and/or wastewater treatment applications. Nevertheless, the effectiveness of FA is highly contingent upon its source and the treatment type it undergoes. One of the factors that determines the composition of FA is the content of the coal that is burnt. FA is predominantly made up of oxides, SiO_2 , Al_2O_3 , Fe_2O_3 , and CaO , with an average of 95% to 99%. Additionally, between 0.5 and 3.5% of FA comprises Na, K, and P, while trace elements comprise the remaining portion [76]. Although the FA composition has been extensively studied, such chemical and mineral content is considerably varied worldwide. The use of FA is anticipated to enhance probable industrial integration possibilities due to the expansion of various uses that may utilize side products and different elements derived from FA. Although FA has been widely used on a lab scale and much less in pilot-scale usage, there have been very limited implementations of FA industrial-scale uses in the water treatment sector. To achieve a successful industrial application, it is necessary to overcome different related issues. Such problems could include large-capacity equipment design, waste and logistics management, and economic obstacles since industrial applications would deal with large amounts of FA material. Therefore, additional research is required to transform FA usage from lab and pilot scales into a commercially viable material with different uses, especially in water treatment applications.

The synthesis of zeolites is becoming increasingly recognized as one of the most efficient ways for FA applications. This may be because FA and natural zeolites have comparable compositions. However, zeolite has a greater surface area, a better capacity for ion exchange, and demonstrates exceptional characteristics of thermal stability [324]. In addition, zeolite has the benefit of being able to adsorb water in a reversible manner without undergoing any change, either physical or chemical, in its structure matrix. Therefore, zeolite is believed to be the most effective method for modifying FA for the purpose of water remediation [218]. In the relevant literature, techniques for converting FA to zeolite included hydrothermal, microwave irradiation, fusion, and ultrasound processes [218,324,325]. Hence, the transformation of FA into zeolite material will enhance its usage on a large scale. Consequently, it is essential to allocate further research efforts towards this application.

FA has several qualities that make it a possible amendment for soils. These properties include a good content of particulates of clay and silt, a reduced mass density, a high water-retention ability, a suitable pH, and the ability to provide important plant nutrients [326,327]. In addition, FA may be used to adjust the soil pH as it is generally alkaline. However, the FA alkalinity highly depends on its source of origin and coal facility working conditions. The use of FA to adjust the pH of soil significantly benefits immense soil areas, such as wastelands, unproductive fields, and mining areas residues. It can bring them to higher levels of productivity [328,329]. FA is also a source of important minerals, including K, Ca, Mg, Cu, and P, all of which are good for the development of plants. Additional advantageous impacts have been identified. These include better soil texture, better airflow, enhanced percolation, less dense soil, less need for other soil amendments, and killing-insect properties attributed to the presence of silica in its content [76,330]. Even though research has been conducted on using FA as a soil amendment, the implementation of such an approach has not yet been put into practice on a large scale. Consequently, further investigation is necessary in this field.

It is generally agreed that the ceramic industries require several metal oxides, such as SiO_2 , Al_2O_3 , and CaO , as raw materials for their processes. As FA is rich in the mentioned substances, the metal oxides present in FA are considered cost-effective materials and readily available for use in the ceramic sector. Furthermore, the tiny particulate nature of FA renders it very compatible for direct and effortless incorporation into ceramic pastes,

requiring little pre-treatment [331]. Based on the temperature activation of the raw FA, some studies have been conducted to examine whether or not stirred materials and glass ceramics could be produced from FA. The fluctuation in temperature and the addition of co-reagents responsible for controlling the ultimate shape of the glass-ceramic is the foundation upon which this manufacturing process begins. Glass-ceramic substances are usually composed of three different materials, namely, Li_2O , Al_2O_3 , and SiO_2 , and are highly promising for industrial use owing to their exceptionally low and negative thermal expansion coefficients. Nonetheless, these substances remain costly due to the utilization of high-grade materials, especially reagents, in their production process [75]. A recent study synthesized a glass-ceramic material using a bottom ash. The study findings revealed that the ash-based glass-ceramic has a thermal expansion coefficient value lowered by only 18% compared to a commercially available glass ceramic [332]. In another study, the preparation of glass-ceramic material was carried out with FA serving as the precursor substance. The study found that the synthesized glass-ceramic exhibits a well-defined crystalline structure with small-dimension particles [333]. For comparison purposes, three different materials, glass, glass-ceramic, and ceramic, were synthesized using FA without adding other substances. The glass-ceramic substance formed from FA exhibited superior microstructural, physiochemical, and mechanical characteristics compared to the glass and ceramic materials generated using FA [334]. Although research has been conducted on using FA as a raw substance for ceramic and glass-ceramic material production, the efforts remain less than expected. Therefore, further endeavors should be undertaken in this promising path of FA research. Such a path would significantly expand FA uses because ceramic and glass-ceramic materials have a wide range of applications.

11. Conclusions

Various forms of wastewater are produced daily due to activities, including households, agriculture, and industries. Water pollution primarily emerges from untreated sewage water, hazardous industrial pollutants, and runoff from agriculture. Industrial effluents often manifest elevated pollutant concentrations among various wastewater types, mainly containing dangerous elements such as heavy metals. These highly toxic pollutants are characterized by their slow degradation. Therefore, eliminating these metals from effluents presents a challenge. Biosorption has risen as a favorable approach with several benefits, including an affordable method, straightforward implementation, and impressive effectiveness, even when dealing with lowered ion levels. In this review, different aspects have been reviewed, focusing on removing heavy metals using an industrial waste material, FA, as an adsorbent. Several related metallic ions contamination issues were evaluated, including causes of pollution, contamination levels, and health effects of heavy metals and their removal approaches. The relevant literature studies on using FA as an adsorbent material in heavy metal decontamination applications were reviewed. Such literature was critically analyzed from different perspectives, and the following points can be highlighted.

- Using FA as an adsorbent, the adsorption process is affected by many factors. Among them, pH significantly impacts the heavy metals removal performance. In general, the removal of heavy metals is improved at lower pH values, especially within the pH range of 2–5.
- Using FA, it was found that the removal rate increases when there are lower concentrations of heavy metals and vice versa. However, the removal rate is influenced by both adsorbate and heavy metal concentration.
- The findings revealed that adsorption temperature positively affects the removal process. However, a negative impact was also registered.
- It is concluded that the carbon content within FA relates to the surface area, resulting in a significant role during heavy metal removal. It was also found that the FA capability is enhanced when higher CaO percentages are within its content.

- It was found that the addition of nanomaterials can lead to enhanced FA's ability to remove heavy metals. Examples of such materials include CaO, CaCO₃, Ag, and Fe₃O₄ nanoparticles.
- It was observed that most heavy metal removal follows the Langmuir isotherm. The Langmuir fit suitability indicates that the adsorbed heavy metals tend to form a monolayer on the FA surface.
- Regarding kinetics removal, it was found that the pseudo-second-order kinetics well describes the removal of heavy metals. However, some metals had a removal behavior consistent with the pseudo-first-order kinetics equation.
- It is indicated that the adsorption process using FA as an adsorbent has two different steps: diffusion within the boundary layer, which is influenced by the external mass transfer impact, and intraparticle diffusion within the adsorbent pores.
- The cost analysis found that using treated FA with physical and chemical treatments is highly cost-effective and can achieve significant savings compared to commercial adsorbents.
- Despite being used in several applications, the ability of FA to undergo a transformation into a zeolite material via specific treatment holds promise for new application areas. Nevertheless, more investigation is necessary to validate this methodology.
- In conclusion, FA is known for its cost-effective origin as a waste material, making it a potentially advantageous resource for water treatment applications and diverse utilizations owing to its significant chemical and mineralogical composition.

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