



Modification of Agricultural Waste Carbon Adsorbents with Iron and Iron Oxide Nanoparticles for Heavy Metals Removal: A Scoping Review of the Literature

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ABSTRACT

Introduction: Considering the damage caused by heavy metal pollution, researchers and environmental health organizations have prioritized developing methods to remove heavy metal ions from polluted water. This study reviews existing literature on the use of agricultural waste, as well as the modification of agricultural waste with iron and iron oxides, for heavy metal removal.

Materials and Methods: The systematic review included a search for relevant literature published between 2000 and 2022 in English, with 50 articles being selected for inclusion. After removal of duplicates and screening for eligibility, thematic analysis was conducted to evaluate the advantages and disadvantages of practical, economic methods for preparing and modifying agricultural waste for heavy metal removal.

Results: A total of 50 articles were selected for inclusion, covering the preparation and modification of adsorbents from cellulose sources and agricultural waste. Thematic analysis revealed that agricultural waste is an environmentally friendly adsorbent with a high capacity for removing cadmium, lead, and arsenic from aqueous solutions. Moreover, modified adsorbents with iron and iron oxide nanoparticles demonstrated superior adsorption capacities compared to their unmodified counterparts.

Conclusion: This review highlights the potential of utilizing cellulose sources, particularly processed fruit waste, as a suitable material for preparing carbon-based adsorbents and modifying their surfaces with iron and iron oxide nanoparticles. Their abundance, adsorption capacity, low cost, and availability make them a promising solution for removing heavy metals from aqueous solutions.

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Introduction

Population growth has led to increased industrial production, demand for raw materials, and significant technological advancements, resulting

in substantial environmental changes. These changes have contributed to ecological pollution and threaten living organisms, either directly or indirectly. Surface and groundwater resources are

vulnerable to pollution. One major source of pollution for these resources is industrial and urban wastewater, which contains various harmful pollutants depending on its type and source. While some pollutants are degradable and easily removed, others, such as heavy metals, are nonbiodegradable and persistent. Examples of heavy metals include Cd, Pb, As, vanadium, Se, Hg, Zn, and Cu. Some of these metals, such as copper, nickel, and zinc, are essential for metabolic processes at low concentrations but have adverse effects on the health of organisms at high

concentrations. Others, such as cadmium, lead, and arsenic, are toxic and accumulate in the human body over time, leading to long-term negative health effects upon exposure¹.

Heavy metal ions are often found in high concentrations in municipal and industrial wastewater. The discharge of industrial wastewater has led to a rapid increase in heavy metal concentrations in the environment, particularly in the surface waters. Table 1 shows the various heavy metals and their combinations found in the different types of industrial wastewater.

Table 1: Presence of heavy metals in different industrial wastewater²

Industry	Heavy metal
Mining	Al, As, Cd, Hg, Mn, Mo, Pb, U, V,
Métallurgie	Ag, As, Be, Bi, Cd, Cr, Cu, Hg, In, Pb, Ni, W, Zn
Chemical industries	Al, As, Ba, Cd, Cr, Cu, Ga, Hg, Os, Pb, Sn, Ta, Tl, Zn
Paint manufacturing	Al, As, Cd, Cu, Pb, Sb, Ti, U, Zn
Jewelry making	Co, Cu, Ga, Hg, Ni,
Pottery	As, Co, Pb, Tl
Alloy manufacturing	Fe, Cr, Ni, Mo, V, Cu, Cd, Pb

Lead is one of the most widely used non-ferrous metals in the world, with an estimated annual global consumption exceeding seven million tons in recent years. In Iran, Pb consumption is close to 100-120 thousand tons per year. The biological effects of Pb exposure vary depending on the concentration and duration of exposure, causing widespread adverse effects on living organisms. In the environment, Pb is known to be strongly connected to particles such as sewage sludge, sediments, and oil³.

Cadmium and cadmium compounds exhibit higher solubility in aqueous solutions than other heavy metals, making them more mobile in soils and increasing their tendency to accumulate in biological environments. Arsenic, used in industries such as glass processing, textiles, paper, pigments, metal alloys, ammunition, wood preservatives, and metal adhesives, is a natural component of the Earth's crust but becomes toxic in its inorganic form.

As arsenic, cadmium, and lead cannot be metabolized, they accumulate in tissues, such as fat, muscles, and bones, causing various health disorders. The accumulation of heavy metals in

plants enables them to enter the food chain, thereby posing an increased health risk. In light of these concerns, environmental protection organizations have recommended limiting the allowable concentration of these elements in aqueous solutions to less than 5µg/L⁴.

With the growth of electronic industries and the rising production and consumption of metals, there is a growing need for effective and economical methods to remove these elements from industrial wastewater before they enter the environment, agriculture, and biological cycles, accumulating in various human and plant tissues. Developing strategies to address this issue is a top priority for environmental science and chemistry researchers. Preventing further contamination of the environment and water resources is crucial for creating a sustainable future.

Various technologies have been developed to remove heavy metals from aqueous solutions, including traditional methods such as precipitation, ion exchange, filtration, electroplating, and coagulation⁵⁻⁷. However, these methods have notable drawbacks, such as high chemical and

energy consumption, formation of hazardous sludge, low separation productivity when heavy metal concentrations are below 100 µg/L, and high application costs on a large scale^{8,9}.

Adsorption is a simple and suitable process with significant potential for pollutant removal from wastewater. Surface adsorption is an attractive method that is widely used in advanced wastewater treatment plants because of its numerous advantages over other treatment methods, such as low cost, high efficiency, minimal generation of chemical and biological sludge, no need for additional raw materials, and the possibility of adsorbent recovery. Many researchers have investigated different approaches to the surface adsorption process to remove low concentrations of organic and inorganic contaminants from wastewater^{10,11}.

Recent studies have focused on using modified adsorbents, particularly those derived from agricultural waste, to replace conventional adsorbents for the removal of heavy metals from aqueous media. This shift was attributed to the remarkable efficiency of the adsorption process. The main advantages of adsorbent modification include the presence of functional groups on the surface, high selectivity, and a strong affinity for heavy metals. Extensive research has been conducted to explore and enhance these benefits for heavy metal removal^{12,13}.

Activated carbon is a broad term that describes carbon-based materials with a highly developed internal pore structure. It is widely recognized as the most commonly used adsorbent for removing inorganic and organic contaminants during wastewater treatment¹⁴. Activated carbon can be produced from carbon-rich materials such as wood, coal, and plant waste. Its unique properties, including a high surface area, high porosity, highly developed internal pores consisting of micro-, meso-, and macro-pores, and a diverse range of surface functional groups, make activated carbon highly versatile and applicable in various fields, particularly environmental industries¹⁵. However, its high cost has been a significant barrier to its widespread use as an adsorbent for pollutant removal.

To address this issue, researchers have turned their attention to agricultural wastes and by-products as alternative materials owing to their many advantages^{16,17}. This includes renewability, low cost, efficiency, availability, and environmental friendliness. Agricultural wastes have shown great potential as sources for removing heavy metals from water and wastewater, primarily because of their surface functional groups¹⁸⁻²⁰.

Agricultural by-products may include different parts of the plant, such as bark, stems, leaves, roots, and flowers. They contain different types of functional groups such as acetamide, carboxyl, phenol, amide, amine, carboxyl sulfhydryl, alcohol, and ester. The hydrogen atoms of their functional groups can be replaced by metal ions in solution or form a complex by donating an electron pair; hence, they have a good ability to bind with heavy metals²¹. The characterization of agricultural wastes and by-products plays an important role in the development of specific adsorbents for industrial applications compared to conventional adsorbents. Recent studies have indicated that the carbonization of agricultural wastes and by-products as adsorbents for the removal of heavy metals has decreased waste from the environment. Hence, these methods are low-cost, effective, and comply with the concepts of waste management²². It is not easy for researchers to search for good adsorbents among various agricultural wastes and by-products. Various researchers have presented results to determine the appropriate criteria for choosing a suitable adsorbent. According to researchers, the availability, abundance, cost-effectiveness, easy disposal, high recycling, and low release of unexpected compounds in aqueous solutions are key factors in the selection of agricultural wastes and by-products for practical applications in the removal of impurities from aqueous solutions. In addition, the adsorption capacity is a determining factor in choosing agricultural wastes and by-products as adsorbent²³. High adsorption capacity is the only important factor in the appropriate choice for the removal of heavy metals in a full-scale process. For this purpose, it is necessary to

modify the chemical structure of the adsorbent so that the adsorption capacity can be increased for the selective removal of heavy metals.

Different methods have been reported to change the surface structure of activated carbon using chemicals to increase the adsorption capacity of adsorbents for the removal of particular contaminants. Surface modification methods are classified into three main categories: (a) chemical, (b) physical, and (c) bio-modification²⁴. It should be noted that surface functional groups affecting the adsorption potential have to be identified before any modification on an adsorbent. This characteristic will help to add groups on the adsorbent surface with specific physical and chemical characteristics to increase the reaction with contaminants in aqueous solutions. Chemical modification of the adsorbent structure for different purposes involves various chemicals such as acids, bases, or metal ions. Generally, acidic modification of carbon is carried out for the oxidization of carbon porous surfaces to enhance the hydrophilic nature of the carbon surface and its acidic nature for the removal of minerals¹². Nitric and sulfuric acid are among the acids compared to some other acids that were considered and used by most of the researchers. Acidic functional groups as functional groups containing oxygen on carbon surfaces were studied to remove heavy metals from water, and it was found that metal ions tend to form stable complexes with the negative charge of acid groups²⁵. Basic modification of the activated carbon surface (alkaline) generates a positive charge, which is useful for attracting negatively charged species. The easiest way to produce porous carbon with basic surface properties is modification with inert ammonia or nitrogen gas at high temperatures²⁶. The modification of activated carbon by NH_3 at 400-900 °C leads to functionalization with basic nitrogen. In general, nitrogen-containing groups create alkalinity that generates dipole-dipole interactions, hydrogen bonding, or covalent bonding between porous carbon functional groups and acidic molecules.

In recent years, modification of the carbon surface using impregnation with nanoparticles,

including metal ions, has been carried out by combining nanotechnology. This review focuses on recent developments in the application of large surface area nano iron and iron oxides to modified agricultural wastes and their applications in removing heavy metals, especially Cd, As, and Pb cations, in water.

Materials and Methods

Search method

The literature search was conducted using five keywords - "adsorption", "heavy metal removal", "impregnation", "agricultural waste", and "iron and iron oxide" - in Scopus, Web of Science, and ScienceDirect databases, covering articles published between 2000 and 2022. Only articles published in English were included in this review. Two independent reviewers evaluated the papers to determine whether they met the inclusion criteria, specifically focusing on various methods of utilizing agricultural residues and their modifications for removing heavy metals from water.

Search outcome

The search strategy yielded 256 articles, and after removing 61 duplicates, editorials, comments, or discussions, title or abstract screening was performed prior to analysis. By applying the inclusion criteria to the titles of articles, 151 articles remained for future analysis. Two independent experts assessed the abstracts of the articles, and 68 articles were excluded. Then, 33 more articles were excluded because they did not provide sufficient detail on the methodological processes or fully evaluate the outcome of the strategy.

Finally, 50 papers focusing on different methods of using agricultural residues and their modification to remove heavy metals from water were analyzed for a full-text review. Fourteen articles were quantitative studies on the use of agricultural waste, and ten articles on iron and iron oxide nanoparticles were selected to provide a complete description. Seven articles were selected to provide examples of related articles on metal removal in the review, which are presented in

Tables 2 and 3. Each method had inherent limitations. Their advantages and limitations were investigated in all articles. Finally, the modification of the adsorbents with iron and iron oxide nanoparticles was evaluated and compared with those of other adsorbents.

Results

The results of this review study are presented in two parts: a) literature review on the application of agricultural wastes for heavy metals removal, and b) a literature review on the modification of agricultural wastes by iron and iron oxide nanoparticles for heavy metal removal. Each section is briefly discussed below:

Use of agricultural wastes for heavy metals removal

In a study conducted by Kelly-Vargas et al. (2012), lemon and orange peels exhibited adsorption capacities 48% and 15% more than banana peels in copper and lead adsorption, respectively. However, Cd adsorption by banana peel was higher than that by lemon and orange peel²⁷. A study by Mosa et al. (2011) indicated that the removal efficiency of heavy metals from wastewater was in the order of cotton stalk > corn stalk > rice straw. They found that the highest removal percentage by cotton stalk was related to the high concentration of hemicellulose, lignin, and cellulose compounds in comparison with other materials²⁸. Osman et al. (2010) reported that the removal efficiency of rice hull, sawdust, sugarcane bagasse, and wheat straw for cadmium ion were 84.84, 82.72, 74.07, and 66.74 %, respectively. Rice hull showed the highest efficiency in removing Cd, Fe, and Zn from aqueous solutions compared to other adsorbents in the bio-sorption process. They suggested that the high adsorption

capacity of rice hull compared to other biosorbents for the removal of heavy metals was probably due to the presence of silanol groups (SiOH) in the structure of the rice hull and the higher surface area of the rice hull²⁰. The adsorption capacities of banana peel, orange, lemon waste, and garden grass as raw materials for copper were in the range of 27.68 - 70.40 mg/g which was similar to or even greater than that of ion exchange resins (26.73 mg/g). Some other types of natural agricultural wastes and by-products, such as Tamarind seed, Watermelon peel, Petal waste have exhibited Cu(II) adsorption capacity, 210, 315, and 364 % times greater than ion exchange resins, respectively. This phenomenon can be attributed to the availability of numerous active bonding sites on the surface of agricultural wastes and by-products which increase binding of heavy metals on the surface²⁹. Although studies have indicated that most agricultural wastes without any chemical pretreatment have high adsorption capacities to remove heavy metals compared to conventional adsorbents, in most cases, chemical pretreatment can highly enhance the potential of adsorbents. For example, the Peanut shell modified by H₂SO₄ has exhibited a very high adsorption capacity (406.6 mg/g) for Cu(II). A noticeable increase in the adsorption capacity of Cu(II) using Peanut shell modified by H₂SO₄ is probably due to the removal of competitive cations, increase in surface area as well as porosity on the adsorbent surface^{19, 30}. Another study determined that adsorption capacity (165 mg/g) for Cr (VI) by raw cotton Coir fiber was relatively high. Coir fiber of cotton grafted by acrylic acid has exhibited even greater Cr(VI) adsorption capacity (196 mg/g)³¹. Similar observations for Cd, Pb, and As heavy metals have been selected and reported in Table 2.

Table 2: Change in the adsorption capacity of modified agricultural wastes in the removal of metal ions from wastewater compared to their unmodified raw counterparts.

Sorbent	Modifier	Metal ion	% Change	Ref.
Wheat straw	Urea	Cd(II)	822.82	32
Orange peel	CaCl ₂ 0.8M, NaOH 0.8M	Pb(II)	84.84	19
Orange peel	HNO ₃ 0.1M	Cd(II)	61.38	33
Parsley	Pyrolysis + FeCl ₃	As(V)	964.16	29
Parsley	Pyrolysis + FeCl ₃	As(III)	416.67	29
Corn cob	180°C Heat treatment and H ₃ PO ₄	Zn(II)	93.96	34
Activated carbon	0.05 M Iron	AS(V)	2.93	35

Nanoparticle modified agricultural wastes for heavy metals removal

Vitela-Rodriguez et al. (2013) tested various activated carbons modified with iron hydro(oxide) nanoparticles for arsenic adsorption from solution. The results of their study indicated that iron content in the modified activated carbons increased about 2% and modification of iron to activated carbons was a good adsorbent for arsenic removal at concentrations lower than 300 µg/L. The increase of arsenic removal after modification of adsorbent was attributed to the formation complex of arsenate anions with iron ions³⁷. The study by Jaber L. et al. (2020) investigated the efficiency of low-cost granular activated carbon (GAC) doped Fe₂O₃ nanoparticles prepared by modified sol-gel technique and used in removal of chromium and lead ions. Their results indicated that activated carbon impregnated by Fe₂O₃ nanoparticles (Fe-GAC) was able to remove about 99% of Pb(II) and chromium aqueous solution³⁸. Monika J. et al. (2018) synthesized iron oxide/activated carbon (Fe₃O₄/AC) by co-precipitation method and studied the removal of Cd(II), Cr(VI), and Cu(II) cations from aqueous solution in a batch process. Their experiments indicated that conditions for the maximum removal of cations were an initial ion concentration of 50 mg/L, adsorbent dose of 5 g/L, pH 6 for Cu (II) and Cd (II) and 2 for Cr (VI), contact time 3 h,

temperature of 25 °C, and shaking rate of 180 rpm. They also indicated that Langmuir model well described the equilibrium data and R² values were 0.97, 0.98, 0.98, and by Fe₃O₄/AC for Cd(II), Cr(VI), and Cu(II), respectively. They studied the effect of temperature in the range of 288–328 K and confirmed that the cations adsorption on the Fe₃O₄/AC was endothermic and these nanoparticles could regenerate after four adsorption-desorption cycles³⁹. George P. Gallios et al. (2017) studied removal of As(V) ions by iron-modified activated carbons as adsorbents from aqueous solutions. They used an efficient and simple process to prepare Fe_{3-x}Mn_xO₄ activated carbons. To this end, carbons were soaked with magnetic precursor solutions and then calcinated at 400°C. The iron impregnation exhibited an increase in maximum As(V) adsorption capacity for raw carbon from 4.3 to 11.05 mg/g, while impregnation of manganese (Mn) further increased the adsorption capacity to 19.35 mg/g⁴⁰. The removal of arsenic from simulated polluted groundwater was studied by adsorption on GAC impregnated with Fe³⁺ (GAC- iron) as well as unmodified GAC in the presence of ions Fe²⁺, Fe³⁺, and Mn²⁺ ions⁴¹. In this case, an increase was obtained in a saturated state of 2.4 % iron ion. Comparison of the adsorption capacity of iron oxides with iron-modified carbon in adsorption of As (III) and As (V) ions is presented in Table 3.

Table 3: Comparison of adsorption capacity of iron oxides and iron modified carbons in adsorption of As (III) and As (V) ions

Adsorbent	Sample	Adsorption capacity		Ref.
		As(III)	As(V)	
Iron oxide coated on sand	Tap water	0.36	-	42
Iron oxide coated on sand	Drinking water	0.41	0.043	43
Iron (III) in resin	Tap water	62.93	55.44	44
Activated carbon + iron + O ₂	Drinking water	-	3.92	45
Carbon modified Iron (III) oxide	Drinking water	4.50	4.5	46
Activated carbon iron (III) oxide	Contaminated water	3.75	4.03	46
Iron oxide on cement	Drinking water	0.67		47
Iron (III) reduction by pomegranate peel	Contaminated water	5.55	7.40	48

The use of appropriate adsorbent in a good adsorption process depends on the surface chemistry and the pores of porous structure. The activation method and the used precursor composition affect pore structure of adsorbent and surface functional groups. In general, oxygen, sulfur, and nitrogen in carbon structure are responsible for the adsorption of pollutants. The surface functional groups significantly affect activated carbon unique adsorption properties. The functional groups on the surface of carbon were derived from activation process, precursor composition, heat treatment, and chemical modification. The nature and number of surface functional groups may be changed by appropriate thermal or chemical modification methods to improve the performance of activated carbon in removing certain contaminants. Continuous efforts were made to improve of carbon surface using different chemicals or physical methods, optimization activation conditions (different factors, temperature, and process time), the use of suitable precursors, additives, etc.⁴⁹. Therefore, the main focus of researchers is to optimize activation methods or surface modification and develop the use of suitable precursors for certain contaminants. In recent years, many studies have been conducted to use fruit peels, due to their remarkable merit, to replace custom adsorbents in heavy metals removal from aqueous solutions. The main advantage of fruit peels over other conventional adsorbents is its high selectivity and strong affinity towards heavy metals due to the abundant availability of binding groups on their surface⁵⁰. Fruit peels are relatively inexpensive or without any cost, readily available,

renewable, and show strong affinity for heavy metals.

Discussion

The analysis of selected papers indicated that agricultural wastes of different materials are suitable for removal of metal ions either in their natural form or after a physical or chemical modification. These materials include wheat bran, rice bran, pollen from different plants, bark of trees, peanut shell, coconut shell, nut shell, walnut shell, cotton seed shell, tea leaf waste, cassia leaf, corn cob stem, sugarcane bagasse, peel of apple, bananas, orange, soybean shell, grape stem, sugar beet pulp, sunflower stalk, coffee beans, arjun nut, cotton stalk, etc.⁶.

Literature indicated that chemical factors affecting adsorption capacity include adsorbate type, adsorbent type, and particularly special conditions in the adsorption process. It seems that the selection of agricultural waste as the processor or adsorbent in the preparation of carbon is very important. It is necessary to determine the adsorption capacity of each item in laboratory studies and research to be economically beneficial. Previous studies have investigated that the adsorption capacity of agricultural wastes and by-products is significantly different. The type of removable pollutant is also very important on the adsorption capacity of agricultural wastes and by-products.

The efficiency of agricultural wastes in the removal of pollutants increases by modifying them, which is reported in literature and briefly mentioned in Table 2. Agricultural waste is used to

make adsorbent and provide activated carbon for agricultural commodities, offer solutions to environmental problems, and help to decrease the waste disposal cost.

Agricultural wastes and by-products can be transformed into effective adsorbents through the carbonization process. Carbonization offers several benefits, such as improved filtration and easier separation, reduced leaching of volatile components into the aqueous medium, mitigation of chemical pollution from substances like dyes and COD, and easier maintenance and storage of the adsorbent materials.

The chemical modification of carbon surfaces was observed to be a promising and attractive method to increase carbon applications in many fields for pollutant removal. The modified carbon

acts selectively and also increase the adsorption capacity to remove heavy metals. An overview of recent developments has been investigated in the preparation of surface-modified activated carbons by saturation of metallic nanoparticles, and the potential of the surface-modified activated carbon has been presented in water purification applications. More information is recommended about the experimental method and modification conditions to study the full articles listed in the references. The saturation by metal ions using nanotechnology has been provided for a good distribution of chemicals or metal particles on the surface of activated carbon. Carbon impregnated with metal ions such as aluminum, copper, silver, and iron has attracted researchers' attention due to the advantages listed in Table 4¹³.

Table 4: Advantages of carbon surface modification by metal ions

No.	Advantage
1	Functionalization of carbon by other elements or their oxide and thus enhancing adsorbent hydrophilic property
2	Change in pH _{zpc} to a more positive charge and thus increasing its applied range for adsorption of cations
3	Increase in functional groups on the surface and thus increasing its adsorption capacity for removal of pollutants
4	Increase in the porosity of activated carbon by changing in the intramolecular bonds
5	Increase of the adsorbent relative weight and thus ease of suspension separation

The impregnated activated carbon with metal ions has indicated an increasing adsorption capacity toward negative ions such as cyanide, fluoride, and heavy metals such as arsenic anions in water. Among the ecofriendly-metal ions are iron salts, which are widely used in the removal of pollutants and have recently been used in the saturation of activated carbon.

Conclusion

In conclusion, converting agricultural wastes into activated carbons offers a promising solution for treating water, wastewater, and polluted aqueous solutions by effectively removing DOM, dyes, and metal ions. Utilizing agricultural wastes in this manner can contribute to resolving environmental issues and reducing waste disposal costs. Given the abundant availability of agricultural wastes, the cost of preparing these carbons is expected to be low, providing a potentially cost-effective alternative to existing

commercial adsorbents.

Agricultural waste and by-product carbons have demonstrated success in removing pollutants from aquatic environments. Therefore, further exploration is warranted to develop more cost-effective and selective sorbents. While there are current limitations, chemically pretreating agricultural waste with iron ions or iron oxide nanoparticles has shown potential for significantly enhancing their metal adsorption capacities. Consequently, more attention should be given to employing nanotechnology methods for preparing nanocomposites.

Further research is required to investigate the performance of these materials in multi-ion systems, high ionic strength solutions, and real wastewater to make the industrial use of agricultural waste and by-product carbons more viable.

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Authors' contributions

MHS and MA participated in study design, conceptualization, project administration, and final editing of the manuscript. MJS and FB performed the search and wrote the original draft. MJS and SK participated in the resources analysis. All authors have read and approved the manuscript.

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