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Assessment of the possibility of using carbon sorbents from biowaste for soil purification from heavy metal ions

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ABSTRACT
Water and soil resources are one of the most important natural resources of a country, from which all the food needs of humans and animals are provided, but unfortunately, they are constantly exposed to encroachment and changes by human and non-human factors. Biochar is one of the solutions recently considered in international scientific forums for soil and water protection. In this study, carbon adsorbents' performance has been investigated to remove heavy metal pollutants. Carbon adsorbents, unlike resins that only deal with ion exchange, work in different environments, including in the presence of carboxyl, imidazole, sulfhydryl, amine, sulfate, phosphate, thioether, phenol, carbonyl, amide, and hydroxyl bases. In this study, the absorption rate of heavy trace elements with carbon adsorption and their efficiency has been investigated, and the results of pH and optimal concentration for carbon adsorption have been presented. A study has been done on the carbon absorbents used to separate heavy metals. Bio-carbon adsorbents are a cheaper and more effective alternative to separate metals and metal elements, especially in the separation of heavy metals in soil treatment. In this study, the amount of absorption in bio-absorbents, according to the cell structure and their types, has been investigated. The results show that the subsequent adsorption of bio-carbon adsorbent can be a suitable method for purifying soil from heavy metal ions.

Keywords: Carbon sorbents, Biochars, Bio-absorbents, Heavy metal, Soil purification
Article type: Review Article.

INTRODUCTION
Environmental limitations, the risk of water and soil crisis, the importance of recovery, and the increase in surface and underground water pollution by heavy metals and other pollutants from sewage, finding effective and economical environmental solutions to eliminate. These materials are essential from water and soil sources. In this regard, using cheap waste can be very helpful (Madeła & Skuza 2021). Bio-carbon residues are the most widely used among bioabsorbents. The advantages of these compounds include low cost, good efficiency, minimum waste and residual materials and can be recycled (Tsade *et al.* 2020). Fruit and vegetable wastes produced in astronomical amounts in agricultural and food industries often cause disturbance in landfills due to high biodegradability. Biological absorption by these wastes can be an effective technique for removing heavy metals from wastewater (Sagova Mareckova *et al.* 2008; Zhou & Haynes 2010; Niazi *et al.* 2016). The increase in industrial activity is always the main reason for most of the problems of environmental pollution and destruction of the ecosystem, and it causes the accumulation of pollutants such as toxic metals. Pollution of soil, underground water, sediments, surface water, and air with dangerous and toxic chemicals creates major problems for both

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humans and the environment, especially heavy metals as dangerous pollutants. Their presence in the wastewater of some industrial processes such as electroplating, metal polishing, metal mining and smelting processes, tanning, chemical production factories, mining, and battery manufacturing causes more environmental problems because their toxicity is reduced even in low concentrations (Hussain *et al.* 2024). Types of heavy metal removal methods include chemical precipitation, ion exchange, solvent extraction, ultrafiltration, reverse osmosis, nanofiltration, and surface adsorption methods, which are carried out with various materials, the most important of which include active carbon, metal oxide, carbon nanotubes and bio absorbents (Ahmed *et al.* 2024). Heavy metals are among the most common pollutants usually found in high concentrations in industrial wastewater, which also damage soils and products. Today, one of the most important environmental issues is the treatment of industrial wastewater, which includes heavy metals such as lead, copper, chromium, cadmium, nickel, iron, zinc, arsenic, manganese, and mercury (Kowalska *et al.* 2020; Abou Hadid *et al.* 2024; Moulaei *et al.* 2024). These pollutants exist in the wastewater of plating, leather, tanning, casting, photography, electronic, paper, mining, plastic, fertilizer, and chemical industries (Kowalska *et al.* 2020). Several incidents have been reported in the field of contamination of surface sources with heavy metals, for example, "Itai Itai" disease, which was related to cadmium contamination in the Jinsu River, Japan (Abou Hadid *et al.* 2024). These metals enter as a solution in water and soil and cause pollution of surface and underground water and soil (Moulaei *et al.* 2024). They also disturb the ecosystems they enter (Sabir *et al.* 2021). The release of heavy metals into the environment, accompanied by industrial development and population increase, is one of the environmental problems in many countries (Farooq *et al.* 2010). Heavy metals can accumulate in living organisms' bodies and cause various diseases and disabilities. These metals are not biodegradable and their toxic effects are chronic in living organisms. There is growing interest in using commercially available and low-cost materials to remove heavy metals. The main advantage of absorption technologies is their effect in reducing heavy metal ions to a very low level using cheap absorbent materials (Wong *et al.* 2018). The use of activated carbon, which is expected, is very costly compared to the safe and economical method of using agricultural residues (Mahato *et al.* 2021). In addition, a wide range of biological materials, especially bacteria, algae, yeasts, and fungi, have received a lot of attention for removing and recovering heavy metals due to their good performance, low cost, and available quantities (Ram *et al.* 2024). Several studies have been conducted in this field in the world, some of these studies are mentioned below. In a study by Patel (2012), the potential of fruit and vegetable residues as new bioabsorbents was investigated (Starodubtsev & Bakai 2021). In another study conducted by Wang & Chen (2009), the investigation of biosorbents for the removal of heavy metals was considered, and the capacity of different biosorbents for the removal of heavy metals was investigated (Lemishko 2018). Other studies have also been conducted in this regard, which can be used to remove heavy metals from wastewater by Vasa *et al.* (2017) using agricultural waste as an adsorbent. Therefore, the purpose of this study is to investigate the use and efficiency of agricultural waste as low-cost adsorbents in the removal of metal and organic pollutants from wastewater and the conditions that lead to maximum absorption of pollutants, as well as a comparison between different adsorbents in the removal of heavy metals and dyes. It is possible to make the most appropriate decision in choosing the absorbent to remove the desired pollutant. It is also possible to prove the effectiveness of low-cost absorbents, such as agricultural residues, in eliminating contaminants and using them as a suitable alternative to expensive absorbents. This paper tries to assess the efficacy of using carbon sorbents from biowaste for soil purification from heavy metal ions.

MATERIALS AND METHODS

Biosorption is a procedure that can be modeled by the liner model based on the absorbent rate, capacity, and time (Staroń *et al.* 2024). The absorption mechanism can be considered as nonlinear;

$$\frac{dq_t}{dt} = k1(q_e - q_t)$$

$$Ln(q_e - q_t) = Lnq_e - k_t$$

Here, qe is the adsorbent's absorption capacity at equilibrium (mg g^{-1}), qt is the amount of material absorbed at time t (mg g^{-1}), and kL is the rate of absorption (min-1).

The Langmuir absorption isotherm, a versatile and widely applicable physical law, is a fundamental concept in adsorption science. It accurately describes monolayer adsorption on surfaces with a finite number of identical adsorption sites, as shown by the following relationship:

$$q_e = \frac{Q_{\max} K_L C_e}{(1 + bC_e)}$$

where q_e is the amount of absorbed pollutant (mg/g) at any moment, Q_{max} is the maximum absorption capacity by the biomass (mg g^{-1}), K_L or b is an equilibrium constant that depends on the amount of the adsorbed to the biomass (1/Lmg), and C_e is the equilibrium concentration of pollutant or not absorbed (1/Lmg). The q_e in terms of Ce is a homographic function where the value of q_e in each Ce can be deduced as

$$q_e = (C_0 - C_e) / X_0$$

where C_0 and C_e are the concentration of the species in the input and output streams, respectively, and X_0 is the consumption dose of biomass, which is: the amount of mass of biomass per unit volume of solution. Longmore's equation is linearized as follows:

$$\frac{C_e}{q_e} = \frac{C_e}{Q_{\max}} + \frac{1}{Q_{\max} . K_L}$$

Soil purification

Soil is vital in transferring pollution as an interface between water and air. Due to the continuous pollution of air and water with pollutants, especially oil pollutants, soil purification services are done in the following ways by using domestic and foreign expert including physical, chemical, biological, thermal, methods of stabilization and stability of pollutants. Each of the above soil cleaning methods can be implemented in two ways: in-situ and ex-situ. The selection of each method depends on several factors, such as the type of pollution, age of pollution, distribution of pollution, width and depth of the soil, etc., which will be determined by the experts of this company, depending on the case. Experts have experienced some of the methods that are more commonly used in cleaning contaminated soil.

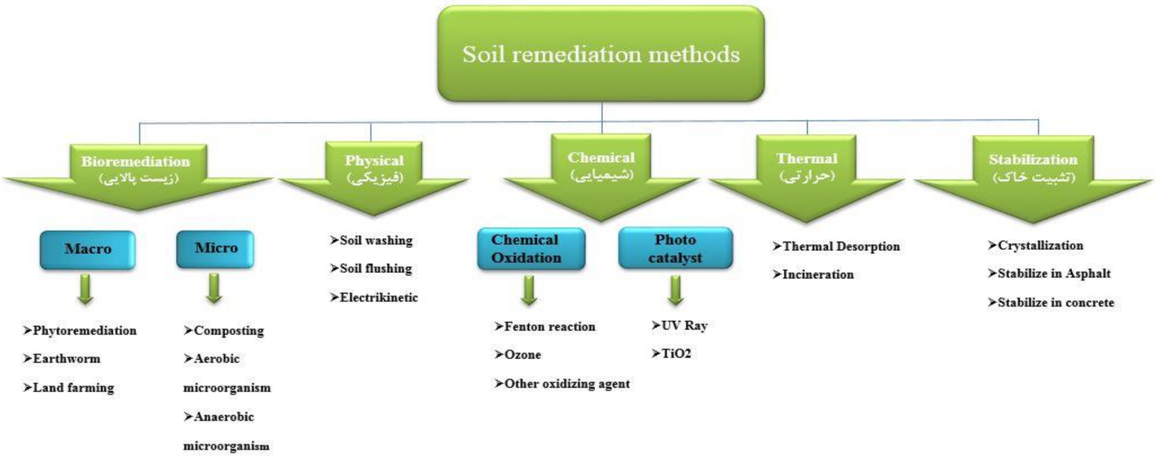

Fig. 1. Soil purification methods [3].

Some of the methods that are more commonly used in the cleaning of contaminated soil and have been experienced by the experts of the Green Sustainable Building Company are as follows:

1. Bioremediation: Biological remediation is a treatment technology that uses the biological activity of living organisms to reduce the concentration or detoxification of pollutants. Generally, microorganisms and bacteria break down or change the form of chemical compounds in the environment in this process. This type of bioremediation is carried out in several ways, including using earthworms, plant cultivation, and composting. The cost of this method is lower than other methods, but the cleaning time is longer. Bio-style soil cleaning methods include biological separation, aeration (aerobic, anaerobic, combined), air spraying, and phytoremediation.

2. Soil washing/soil flushing: This method is included in the category of physical methods. The basis of the operation of this method is the injection of chemical solvents (surfactants) into the soil network and the exit of the pollutant from the soil phase to the water phase. In the on-site implementation method, 2 boreholes are drilled on both sides of the pollution plume, from one of which the detergent enters, and from the other, the contaminated wastewater exits. The effluent will be treated at the ground level in the next step. Although this method has led to good results for some pollutants, experience shows that the decontamination rate in this method is very good at the beginning of the operation, but this rate decreases over time. This phenomenon is called the trailing effect because the pollutant concentration does not reach zero, and a certain amount always remains in the soil.

3. Fenton Reagent: Fenton's method is based on using hydrogen peroxide (H_2O_2) and iron II and III salts. In this treatment process, H_2O_2 and a source of Fe^{+2} ions produce hydroxyl radicals in situ, which continue to degrade organic pollutants in the soil. This method is considered one of the chemical methods and has a higher efficiency than other methods, especially for removing heavy polycyclic hydrocarbons (PAH). In this method, iron salts are a catalyst for producing hydroxyl ions (OH^-), which attack heavy pollutants, break them down, and make them harmless.

4. Oil absorbents: Booms and oil absorbers are plates that physically absorb oil. These plates or pads are oleophilic and hydrophobic. Therefore, these absorbent plates can be used on land and at sea when oil spills occur, such as the overturning or sinking of oil tankers or trucks. Even if these plates and canvases are thrown into the sea or a water tank, they only absorb up to 17 times their weight in oil and stand on the water and do not absorb water. After cleaning the soil and water, these plates can be collected, and the oil can be discharged in a suitable place. These pages can be used many times.

RESULTS

Carbon is undoubtedly the most popular adsorbent and is widely used in wastewater treatment plants around the world. Before today's biological carbon, charcoal or agricultural products were used as water and soil purification absorbents. Biocarbon is produced by the dehydration and carbonization of raw materials and then its activation. The obtained product is known as biocarbon and generally has a very porous structure with a large surface area of 600 to 2000 m^2/g. Biocarbon is a multifunctional adsorbent that can absorb various pollutants such as metal ions, anions, dyes, phenols, detergents, antiperspirants, chlorinated hydrocarbons, and many other chemicals. Due to its availability and low cost, biocarbon can absorb a wide range of heavy metals.

Using agricultural residues in removing metal and color from water and wastewater

Agricultural products, especially those containing cellulose, can absorb various pollutants. The main components of agricultural residues include hemicellulose, lignin, lipids, proteins, simple sugars, water, hydrocarbons, and starch. Among the prominent characteristics of agricultural wastes are economy, compatibility with the environment due to the unique chemical composition, availability in large quantities, renewable, and low cost, which have made these materials an option proposed for water and wastewater treatment. Agricultural residues are a rich source for producing activated carbon due to the low amount of ash and suitable hardness (Kumar *et al.* 2024). As a result, turning agricultural waste into low-cost absorbents is a safe alternative to solve environmental problems and reduce costs. There are different estimates of the amount of agricultural waste in the world. In the latest estimate of Zhou & Haynes (2010), agricultural waste was 18.85%, 15.3 million tons of the total 85 million tons of agricultural production. The increasing trend of food waste is a severe challenge for most countries, especially developing countries. For this reason, politicians and thinkers of scientific societies in the third world are trying to reduce the waste of agricultural products in the stages of planting, harvesting, distribution, and consumption. About 25% of oil revenue is lost every year in agricultural waste, so the neglect of conversion and complementary industries has caused the equivalent of 15 million people's food to be lost every year due to agricultural waste. One of the solutions to reduce the wastage of resources is the possible reuse of these wastes (Sabir *et al.* 2021; Abou Hadid *et al.* 2024). Here, the wastes used as absorbents in the water and wastewater treatment process are mostly the wastes of the harvesting and processing stages, which are referred to as agricultural wastes.

Removal of heavy metals using biological carbon from agricultural residues

There are different types of agricultural waste that can be used to remove heavy metals from water and wastewater. Among the wastes that are very useful in this regard, we mention leaves, stems, kernels, skins, fruits, etc., and each of these wastes can be used to remove heavy metals. Among the heavy metals, the most removal of chromium, copper, nickel, lead, zinc, cadmium, mercury, and cobalt, respectively, by rice bran, orange peel, coconut fiber charcoal, orange peel, pistachio peel charcoal, banana peel, charcoal, Almond skin, and compost tea happened. Finally, among the following agricultural wastes, the highest absorption efficiency was related to rice bran, green pistachio peel, and orange peel, with an efficiency of more than 99% absorption of heavy metals, and the lowest absorption efficiency occurred in pomegranate peel with 55% removal. Two main factors affecting the absorption rate are pH and capacity, as shown in Fig. 2.

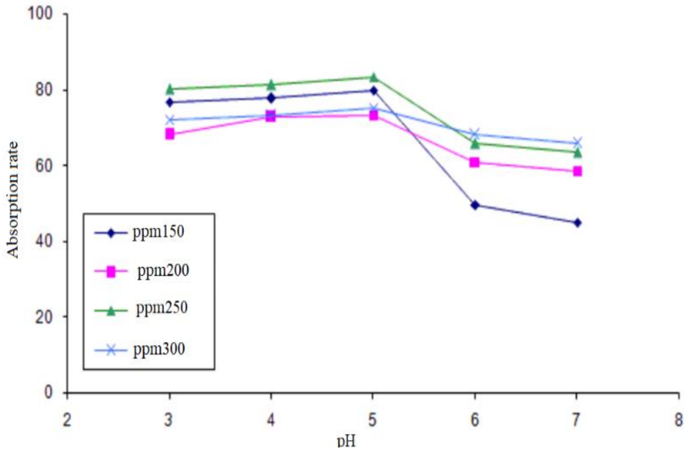

Fig. 2. pH changes in the rate of adsorption of heavy ions with carbon.

Fig. 3. presents the linear model of absorption. Because the surface of most absorbents has a negative charge, the ionization phenomenon increases the absorption speed. Since H^+ and OH^- ions are strongly absorbed on the surface, they can change the surface charge of the absorbent. At low pH, H^+ ion competes with metal ions, and the absorbent sites are occupied by H^+, and metal ions are less close to the absorbent due to the repulsive force. The adsorbent surface gets more negative charge at higher pH and metal ion absorption increases. By the rise in pH, first an increase and then a decrease in the absorption efficiency is observed, because hydroxide complexes are formed by the elevation in pH, and most of them are insoluble and precipitate (Staroń *et al.* 2024). As shown in Fig. 4, the rate of abstraction for various carbon concentrations is presented, and by upraising the concentration, the rate of qe will be elevated.

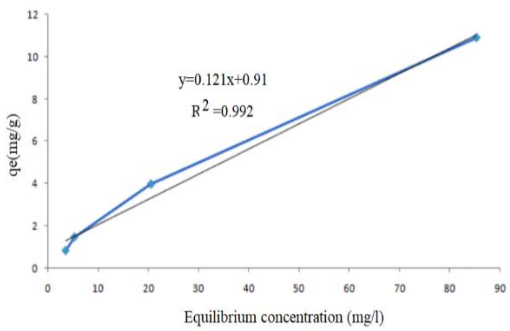

Fig. 3. The amount of absorption based on changes in the equilibrium concentration of carbon.

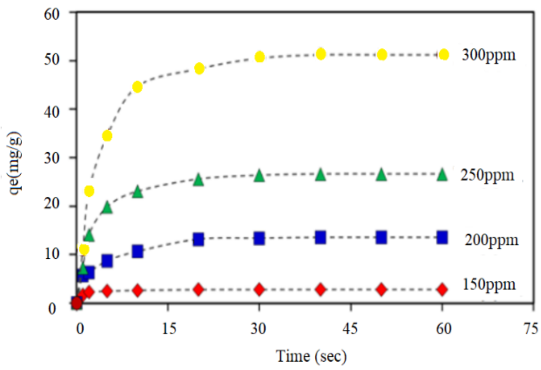

Fig. 4. The effect of carbon concentration on ion absorption.

Among the investigated sources, in the case of heavy metals, the highest absorption efficiency is related to lead, zinc, and cadmium, with an absorption efficiency of more than 99%, and the lowest is related to copper, with 55% removal, presented in Table 1. Most of the materials used have been made in acidic environments, and usually, by increasing the pH, a higher efficiency has been achieved. In most studies, pH 6-8 was the optimal pH for absorption. Most studies have shown that agricultural waste materials in their natural or modified form are highly efficient in removing cadmium metal.

Table 1. The capacity or efficiency of Biological carbon adsorbent in removing heavy metals.

No.	Absorbing	Concentration (mg L^{-1})	Absorbent dose (g)	Optimal pH	Absorption efficiency (%)	Absorption capacity
	Cr	10	0.1	8	97	17
	Zn	10	1	5	98.6	18
	CU	20	8	6	98	15
	pb	50	1.5	5.5	91	18.5

Most of the studies using different doses of carbon to remove chromium have shown variable removal percentages from 99 to 60%. In most of the research, absorption has been done in the acidic pH range, especially in pH below 3 and mostly in pH 2. As a result, pH has a decisive role in the amount of chromium removal.

CONCLUSION

Carbon-based bioabsorbents have a very low cost and are available and renewable. In some studies, the modification of these adsorbents can increase their efficiency. Using low-cost adsorbents to remove heavy metals from the soil seems reasonable and logical because they are relatively cheap or readily available. In other words, they are easily accessible, renewable, and tend to absorb paint and heavy metals. One of the most essential features of the absorbent surface is the porosity and size of the absorbent surface. These two characteristics can be determined from the images - Scanning electron microscope and transmission electron microscopy. The higher the porosity and the size of the absorbent surface, the higher the surface absorption efficiency. Regarding absorption conditions, it is possible to pay attention to conditions such as adsorbent pH, temperature, and heavy metal concentration, each of which can cause a change in the adsorbent efficiency during absorption. Therefore, by changing the above conditions, the absorption efficiency of agricultural waste can be optimized. At the end, it can be said that the removal of heavy metals by the carbon bioabsorbent due to the process of surface adsorption occurred in the range between 55% for the minimum and 99% for the maximum, and the above numbers can be a green light for the use of carbon adsorbent to remove heavy metals from the soil on a large scale.

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