Using Pistachio Agricultural Waste to Remove Environmental Pollutants: A Review Study

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Abstract

Introduction: Agricultural wastes are low-cost absorbents which play an important role in removing waste disposal costs and also in helping to protect the environment. This investigates the efficiency and absorption capacity of various types of adsorbents obtained from hard pistachio shells in removing hazardous pollutants.

Materials and methods: The present study is a systematic review which examined articles related to the use of agricultural wastes obtained from hard pistachio shells as absorbents to remove pesticides, drugs, and dyes in various websites such as PubMed, Google Scholar, Scopus, ISI Web of Science published from 2010 to 2020.

Results: Adsorbents obtained from the hard shell of pistachio have been considered an adsorbent for water purification for many years. Given the physical and chemical properties of pistachio shell such as high absorption capacity, the presence of various special functional groups, and the modifiability of its structure, it has shown a remarkable performance in removing a wide range of pollutants by the surface absorption method. The obtained results showed that the absorption capacity of the adsorbent could be increased by using temperature processes, chemicals and waves. It was also found that the adsorption process using pistachio shell follows the Langmuir isotherm and the pseudo-second-order kinetics in all cases.

Conclusion: Pistachio waste has a good performance as an absorbent to remove pollutants and can be used raw or modified in water and wastewater treatment. Also, the results showed that pistachio shell is a good precursor for the production of activated carbon.

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1. Introduction

Due to its lower initial cost, simplicity of operation, and the impossibility of producing secondary harmful substances, the absorption process is the preferred method of water and wastewater treatment. Surface absorption is a process of material mass transfer. In other words, surface absorption is the accumulation and concentration of materials on a surface that is considered as an absorbent. Extensive efforts have been made to develop cheap absorbents using agricultural, industrial, and urban wastes. Using agricultural wastes as absorbents is desirable due to their contribution in reducing waste disposal costs and helping to protect the environment [1]. Recently, research has focused on the use of natural adsorbents, which are able to remove pollutants from water or wastewater at low cost. In fact, cost is an important parameter in comparing absorbent materials. An adsorbent is considered low-cost if it requires little processing, is abundant in nature, or is the by-product of or waste from industry [2]. Some waste products from industrial and agricultural operations are natural materials which can be considered as potential cost-effective alternative biosorbents [3].

Agricultural residues are considered low-cost surface adsorbents because they are cheap, found abundantly in nature, require little processing, and are effective materials for absorbing pollutants. They include materials such as corn wood, sugarcane bagasse, sugarcane kernel, rice husk, coal, waste newspaper, sewage sludge, wood sawdust, charcoal, bituminous coal, straw, etc. [4]. Agricultural wastes are cheap and renewable sources of activated carbon. These waste materials have little or no economic value, and their disposal often causes difficulty. Therefore, special attention should be paid to these low-cost products [5]. Among the adsorbents investigated in the past, it can be seen that increasing attention is being paid to agricultural residues (raw or activated materials), especially since they are cheap, available almost everywhere in the world, and need only one or a few preparation steps. Therefore, using agricultural waste to absorb pollutants, in line with the principles of a sustainable society, can significantly reduce production waste [6]. Adsorbents obtained from agricultural residues have been used to remove various types of pollutants including dyes [7], heavy metals [8], pesticides [9], and other hazardous pollutants [10].

Iran is one of the largest producers of pistachios in the world. The hard shell of pistachio is one of the most important agricultural by-products in this sector, which is produced after peeling fresh pistachios. This by-product is considered as agricultural waste, and its management has also received the attention of many researchers. On the other hand, the absorbent obtained from the hard pistachio shell contains a mixture of mineral and organic substances. The composition of the pistachio hard shell has various functional groups such as hydroxyl, carboxyl, amino, and nitro on its surface [11].

On the other hand, healthy human beings are the pillar of sustainable development, and human health depends on healthy drinking water. Therefore, healthy and safe water is of great importance. Today, more than 700 types of emerging pollutants in water environments have been listed by the European Environment Agency. Emerging pollutants can be emitted from point pollution sources such as urban and industrial treatment plants and emission sources through atmospheric deposition or animal

husbandry and agriculture. Given the role of controlling pollution in creating a sustainable environment, such a review is of paramount importance [12, 13].

In general, pesticides are substances or mixtures of substances used to prevent, destroy, or control pests, including carriers of human and animal diseases or unwanted plant species [14]. Improper use of these materials without taking environmental considerations into account has caused water sources to be contaminated with pesticides. Dizziness, headache, double vision, eye and skin problems are among the short-term effects caused by pesticides, and long-term effects include respiratory problems, memory impairment, neurological problems, liver problems, infertility and, in some cases, cancers [15]. According to EU regulations, a maximum concentration of 10 mg/L for a specific active substance and 50 μg/L for the total sum of pesticides in water should be observed [16].

On the other hand, due to the spread of diseases and advances in medical and pharmaceutical sciences, the production of drugs has increased in recent years [17]. Medicines, including antibiotics, are not completely absorbed and metabolized after being used, and an important part of them is excreted into the environment in the form of metabolites through urine and feces [18]. The presence of medicinal substances in water sources causes allergic reactions, symptoms of hypersensitivity, including anaphylactic shock, nausea and, in high concentrations, it also causes severe side effects, including liver enzyme disorders, hepatitis, jaundice, blood disorders, etc. [19].

Dyes are pollutants mainly used in the production of cosmetics, leather, paper and in textile industries [20]. Disposing of wastewater containing colored substances causes serious environmental problems such as water pollution, toxicity, allergenicity, genetic mutations, disruption of photosynthesis activities in aquatic environments, eutrophication, aquatic animal mortality, and also aesthetic issues [21]. Therefore, it is essential to remove the pollutants that cause these problems. Considering the characteristics of hard pistachio shell and its production rate in different cities of the country, studying and planning to determine the optimal use of its potentials seems necessary. Therefore, this study examines the removal efficiency and absorption capacity of the adsorbents produced from hard pistachio shells in removing dangerous pharmaceutical pollutants, dyes, and pesticides.

2. Methods

The present study is a systematic review. In order to find all the published studies related to using pistachio residues to remove dyes, pesticides, and pharmaceutical pollutants, various databases such as PubMed, Google Scholar, Scopus, ISI Web of Science with a time limit from 2010 to 2020 were reviewed. The keywords obtained from studying the articles in this area as well as the database of subject titles were used in searching the databases. The keywords included: pistachio, agricultural waste, agricultural waste shell, waste, adsorption, removal, dyes, antibiotic, pharmaceutical compounds, pesticides, insecticide, herbicide, and pollutants. Also, the references listed in all articles published in this area were checked to included other potential sources in our study and to ensure the comprehensiveness of our references.

3. Results

The hard pistachio shell can be used as an absorbent in several ways. In using raw hard pistachio shell as an absorbent, the absorbent is not subjected to any thermo-chemical process and is only ground and used in terms of size and

granularity [22]. In general, the adsorption capacity and porosity of the adsorbent can be increased through a physical, thermal, or chemical activation method. Chemical activating agents usually act at very high temperatures to produce high specific surface area adsorbents [23]. A variety of chemical activating agents have been used, including acids such as sulfuric acid, hydrochloric acid, nitric acid, and alkaline substances such as sodium hydroxide, potassium hydroxide, and oxidizers such as hydrogen peroxide, and potassium permanganate. Physical activation using carbon dioxide or steam has also been reported for the pistachio adsorbent [24].

According to Table 1, the investigations showed that the hard pistachio shell has a high absorption capacity, and the maximum absorption capacity of the hard pistachio shell was reported to be 1276 mg/g in the removal of iodine paint in the reviewed studies [25]. Also, the absorption capacity of the ash obtained from the hard shell of pistachio has been reported to be 327 mg/g [26]. In the following table, the absorption capacity of absorbents obtained from pistachio agricultural residues in removing various pollutants is shown.

Table 1. The absorption capacity of absorbents obtained from pistachio agricultural residues

Pollutant	Adsorbent	Adsorption Capacity (mg/g)	Ref
Methylene Blue	Sawdust of pistachio tree	70.3	[27]
Nitrate	Activated carbon prepared from hard pistachio shells	211.6	[28]
Reactive Red 11	Sawdust of pistachio tree	52.7	[29]
Tetracycline	Pistachio shell powder	98.7	
Amoxicillin	Pistachio shell powder	132.2	[30]
Ciprofloxacin	Pistachio shell powder	92.4	
Tetracycline	Pistachio shell	95.1	[31]
Methylene Blue	Pistachio shells	321.0	[25]
Iodine	Pistachio shells	1276	
Dimethyl Sulfide	Modified activated carbon from pistachio shell	31.2	[3]
Toluene	Alkylation modified pistachio shell-based biochar	169.9	[32]
Ethyl Acetate		96.7	
Reactive Red 238	Pistachio seed shell	81.4	[33]
Methylparaben	Activated carbon derived from pistachio hull	55.5	[34]
Pylparaben		50.1	
Phenol	Pistachio hull ash	327.6	[26]
Brilliant Green	Sulfuric acid modified pistachio shells	151.5	[35]

The review of the studies showed that the absorption process using the adsorbents produced from hard pistachio shell follows the Langmuir isotherm and pseudo-second-order kinetics in all cases. The isotherm models, the maximum removal efficiency, as well as the optimal conditions of the reviewed studies including temperature, the amount of adsorbent, reaction time, and pH are shown in Table 2 below.

Table 2. Review of kinetics and isotherm studies under optimal conditions of the studies

Pollutant	Isotherm Model	Kinetic Model	Removal (%)	pH	Temp (°C)	time (min)	Dose (mg/L)	Ref
Rhodamine B	Langmuir	second-order	41.86	-	30	5	250	[36]
Brilliant blue	Langmuir	second-order	73.60	7.0	20	45	600	[37]
Basic blue 41	Langmuir	second-order	95.54	9.0	50	-	500	[38]
Tetracycline	Langmuir	second-order	95.06	4.0	20	-	80	[31]
Ciprofloxacin	Langmuir	second-order	98.72	5	25	120	100	[30]
Amoxicillin	Langmuir	second-order	-	5	25	120	100	
Pylparaben	Langmuir	second-order	-	6	-	60	60	[34]
Phenol	Langmuir	second-order	98.28	5	25	60	300	[26]

4. Discussion

The review of the conducted studies showed that the preparation conditions of the adsorbent play an important role in the properties of the obtained adsorbent. Physical preparation through crushing and grinding (reducing absorbent particle size) has the least effective role among methods of adsorbent modification. However, if the dimensions of the absorbent particles are in the order of nanometers (nanoparticles), their pollutant removal capacity and efficiency will increase tremendously. The important point is that grinding and crushing are not the only methods by which the pollutant removal capacity of the absorbent can be increased [22]. Using chemicals is the most common method of modifying the absorbent. The reason for this is the reduced modification and also the fact that the chemicals used for modification are often effective even in low concentrations [22].

The reason for this is the reduction of modification time, and in addition, the chemicals used for modification are often effective in low concentrations [22]. In modification with chemical substances, the functional groups of the absorbent are usually strengthened, and some chemicals (oxidizing substances) increase the porosity of the absorbent and thus increase the capacity and efficiency of the absorbent [24]. Temperature and reaction time play an important role in the modification process because they determine the rate of thermal degradation and the evaporation of volatile substances in the adsorbent, which in turn affect the adsorption capacity. In addition, it affects the final carbon content (resistant carbon), atomic ratios, and other properties of the activated carbon. Nitrogen gas blowing conditions and vacuum conditions result in different properties of the obtained carbon.

If vacuum conditions are used, the absorption capacity and carbon content will increase. This will affect the removal efficiency and increase

the efficiency. Also, the reviewed studies showed that the simultaneous use of physical and chemical methods in modifying the adsorbent has a synergistic effect in improving the absorption capacity [22]. Activation using microwaves is a safe and alternative process for the production of activated carbon from agricultural residues, a method which has not been reported for residues from pistachio shells [25].

Studying isotherms can explain how the adsorbed substance reacts with the adsorbent. In fact, studying isotherms has established a link between the pollutant concentration in the solution and the amount of pollutant absorbed on the surface of the solid phase, when both phases are in equilibrium. The adsorption isotherm predicts the adsorption mechanism, especially the distribution of molecules on the surface of the adsorbent that occurs during the adsorption process [39]. Adsorption control mechanisms depend on physical processes such as electrostatics (dipole–dipole interactions and van der Waals forces), hydrogen bonding, or chemical adsorption. Surface adsorption equilibrium is usually described by the isotherm equation. Although there are several isotherm models to evaluate adsorption equilibrium, the two isotherm models by Freundlich and Langmuir are more important [40]. According to the Freundlich model, the absorption layer consists of a molecular layer and all the absorption sites have a single layer absorption with the same absorption energy, and after absorbing one unit, it reaches the saturation limit and there is no interaction between the absorbed molecules. The Langmuir model shows that the adsorption surface is completely smooth and homogeneous. The model is valid for the case of monolayer adsorption on an adsorbent surface with limited and identical adsorption sites [39].

Adsorption kinetics is used to determine the control mechanism of surface adsorption processes such as surface adsorption, chemical reaction, or permeation mechanisms. In fact, kinetic equations are used to explain the transfer behavior of molecules of the adsorbed substance in the unit of time or to investigate the variables affecting the reaction rate. In the first-order model, it is assumed that the rate of change of solute removal with time is directly proportional to the change in saturation concentration and the amount of absorption of the adsorbent with time [41].

5. Conclusion

Given that pistachio is one of the main agricultural products in Iran and the Middle East, the agricultural waste from the pistachio shell can be used as a key source in the development of absorbents for water and wastewater treatment. Adsorbents obtained from the pistachio shell have high removal efficiency (more than 90% in most cases) and adequate adsorption capacity to remove pollutants. The simultaneous use of physical and chemical methods to modify the absorbent has a synergistic effect in improving absorption capacity. The maximum absorption capacity of the hard pistachio shell has been reported to be 1276 mg/g in removing iodine paint and the lowest absorption capacity to be 31.2 in removing methyl sulfide. Most of the reviewed studies show that the absorption process on pistachio residues is of the single layer type. It can be stated that the agricultural waste obtained from the pistachio shell is effective against most polluting species. Agricultural waste from pistachio shells can be recommended as an effective method to replace expensive absorbents. In addition, using these wastes in such a way can play an effective role in cleaning the environment from them, which is significant

from an environmental point of view.

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Conflicts of interest

The authors declare that they have no conflict of interest regarding the publication of the current paper.

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