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Using Hazelnut Shells to Remove Pollutants from Aqueous Media (a Literature Review)

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Abstract: The data on the use of hazelnut (*Coryllus avellana* L.) shells as sorption materials to remove various contaminants (metal ions, dyes, antibiotics) from aqueous systems is summarized in this work. It presents a summary of the literature on the structure, volume of cultivation, and chemical composition of certain hazelnut biomass components. The paper reveals the composition of the hazelnut shell, consisting of lignin, cellulose, hemicellulose, tannins, and proteins, which include various functional groups. The paper provides the data on the ability to remove metal ions (As^{3+}, Al^{3+}, Cd^{2+}, Co^{2+}, Cr(III) and Cr(VI), Cu^{2+}, Fe^{2+}, Hg^{2+}, Li^{+}, Ni^{2+}, Pb^{2+}, and Zn^{2+}), dyes, and antibiotics from water media. It shows the possibility of increasing the sorption characteristics of pollutants by treating the hazelnut biomass with various chemical reagents. It was found that the adsorption isotherms of pollutants on the hazelnut shell are most often more accurately described by the Langmuir models, and the process kinetics mainly corresponds to the pseudo-second-order model. It has been shown that hazelnut shells are a good precursor for activated carbon production, which is effective for removing metal ions, dyes, and antibiotics from aqueous media.

Keywords: hazelnut shell; metal ions; dyes; antibiotics; adsorption; models of adsorption isotherms; thermodynamic parameters; carbon.

1. Introduction

The pollution of the world's oceans with various pollutants resulting from industrial production is currently becoming catastrophic. One of the effective ways to remove pollutants from waste and natural water is the sorption method, based on the absorption of various substances by a developed surface from liquid or gaseous media. However, the activated carbons used in production have several significant disadvantages, such as high cost, selectivity for absorbed pollutants, and the need for regeneration, which significantly increases the cost of the process.

The solution may be rapidly and globally developing an innovative method of using industrial and agricultural waste as reagents for removing various pollutants from water environments [1-11]. Of particular interest are lignocellulose-containing wood processing waste (sawdust, shavings, wood chips) [12-15] and wood biomass components (bark, leaves, needles, cones, fruit shells, etc.) [16-20].

Plant processing produces huge amounts of seeds and shells of fruits annually, which have a hard texture and, in this regard, do not decompose for a long time in the environment, in contrast to pulp and peel. This results in accumulating a huge amount of seeds and shells of tree fruits on a global scale. Previously, we have shown that the latter is a source of valuable chemicals and can be used in many industries, including water purification from pollutants. In particular, it was previously shown that effective sorption materials for removing pollutants from waste and natural water could include the shells of chestnuts [21], walnuts [22], and almonds [23].

One of the fruits with kernels widely used in the food industry is hazelnuts - Hazel (*Corylus*) shrub species in the Birch (*Betulaceae*) family. The nuts of large-fruited forms of a filbert, mainly common hazel (*Corylus avellana*), filbert (*Corylus maxima*), and Caucasian filbert, are called hazelnuts. The fruit of filbert is a single-seeded, almost spherical, or somewhat elongated nut with a woody pericarp. The fruits are clustered by two to eight, sometimes single. Each nut is surrounded by a tubular incised covering, the so-called cup, which originated from a bract and two bracts (stipules) of a female flower. The fruit coat is light green, pubescent, cyathiform or bell-shaped, open, almost the same length as the nut consists of two irregularly dissected laciniate leaflets.

The Food and Agriculture Organization (FAO) estimates that in 2019, more than a million tons of hazelnuts (in their shells) were produced globally. More than half of all nuts contain a shell, making HS a significant by-product of the hazelnut business. Turkey accounts for 67% of global output, followed by Italy, Azerbaijan, the USA, China, and Georgia [24].

The complete chemical characterization of hazelnut shells was made, and cellulose, hemicelluloses, lignin, ash, tannins, and proteins were determined. Chemical analyses revealed that hazelnut shells are composed of lignin (30.2%), cellulose (28.9%), hemicellulose (11.3%), tannins (18.2%), and proteins (6.7%). The chemical composition of the ash (27.7% K and 16.9% Ca) makes them a possible substitute for feldspar in the ceramic industry. XRD showed that the hazelnut shell has cellulose fibers with high-quality crystalline (69.1%) cellulose [25].

Regarding this, HS is a plentiful and affordable raw material with plenty of potential in biorefineries, where it may be used to create a range of high-value products [26]. In particular, it has been shown that HS is a source for the isolation of various oligosaccharides [27, 28], furfurol [29], polyphenolic compounds [30], and other valuable products. HS can potentially be used for dyeing wool and fabrics [31], as a filler for rubbers [32], in the production of lignocellulose composite materials [33], MDF [34], chipboard [35], and other industries.

One of the ways to use HS biomass is to use the latter as sorption materials for the extraction of various pollutants from aqueous media.

2. Use of Hazelnut Processing By-products to Remove Heavy Metal Ions from Aqueous Media

There are many international publications on extracting heavy metal ions from simulated solutions and wastewater individually or in a mixture [36-55] using HS. For the convenience of interpreting the material, the information is arranged in alphabetical order of chemical elements.

In particular, modified HS ($FeCl_3$ and $FeCl_3$ + NaOH) were used to remove As(III) ions from aqueous solutions. It is indicated that temperature 20°C and solution pH = 9.0 are the optimum conditions for adsorption. The maximum adsorption experimental capacities of HS that were treated with $FeCl_3$ and $FeCl_3$ + NaOH were 4.37 and 11.84 mg/g for arsenic ions, respectively. The adsorption data at optimum conditions were analyzed by different isotherm models. It was discovered that the Freundlich isotherm model gives a better fit. Adsorptions are physical because the ΔG° for both adsorbents were found to be lower than 20 kJ/mol [37].

Batch investigations looked into the possibility of employing the shells of HS to biosorb Cr(VI) ions from aqueous solutions. The diluted chromium solutions reached equilibrium within 100 minutes, according to kinetic studies. The pH of the chromium solution affected the HS's ability to absorb metal, with a pH of 3.5 being ideal. The maximal Cr(VI) ion sorption capacities of the sorption process were 8.28 mg/g, which was in accordance with the Langmuir isotherm. At a concentration of 0.5 mM, the percentage of removal by HS was 88.46%, respectively [38].

Composite adsorbents were synthesized by coating citric acid-modified HS with chitosan. Cr(VI) adsorption performances of chitosan-citric acid-modified HS composite (C-CA-HS) were investigated. The optimum adsorbent dosages for the adsorption of Cr(VI) from the 55 mg/L Cr(VI)solution using C-CA-HS adsorbents were d 1.0 g/L, and the optimum contact time is 120 min; the optimum pH is 2.0. The adsorption equilibrium was found to be more compatible with the Langmuir isotherm. For C-CA-HS, the highest adsorption capacities determined by Langmuir isotherm were 89.5 mg/g. Following kinetic calculations, adsorption was compatible with the pseudo-second-order kinetic model (R^2 = 0.9987) as a result of the calculation of thermodynamic parameters; it was determined that adsorption was spontaneous endothermic [39].

Native HS was also studied as a sorption material for removing Cu^{2+} ions from simulated solutions. It was found that the optimum pH value was pH = 6, and the equilibrium time was 120 min. Cu^{2+} ion sorption capacities up to 6.65 mg/g were consistent with the Langmuir isotherm during the sorption process. At a solution concentration of 10-3 mol/L, the percentage of Cu^{2+} ions removed was 75.6%. The outcomes showed that one of the main adsorption methods for tying Cu^{2+} ions to the HS is chelation and ion exchange [40]. The isotherm data seem to fit the Langmuir isotherm model more closely than the Freundlich isotherm model. The second-order kinetic model's correlation coefficients are more than 0.99, demonstrating the applicability of this kinetic equation and the second-order nature of the copper ion adsorption process on HS. Using the information from adsorption isotherms at various temperatures, thermodynamic quantities such as ΔG (−26.87, −27.24, −27.60 and −28.45 kJ/mol for 25, 35, 45, and 60 ◦C), ΔH (+13.58 kJ/mol) and ΔS (44.31 J/mol·K) [41].

HS is suggested as an adsorbent to remove Fe^{3+} ions from aqueous solutions. The removal of Fe^{3+} was examined in relation to the adsorbate's starting concentration, initial solution pH, temperature, contact time, and the adsorbent amount. Under optimum conditions (pH= 3, adsorbent amount 0.6 g, temperature 30°C, time 70 min), the maximum removal of Fe^{3+} ions was 83.5%. Both the Langmuir and Freundlich isotherms were suitable for describing the adsorption of Fe^{3+} ions on HS. The capacity of the HS for adsorption of Fe^{3+} ions was 13.59 mg/g [42].

To create a novel biosorbent for the recovery of Li^+ from an aqueous solution, HS was phosphorylated. The equilibrium sorption capacity was 6.03 mg/g under ideal circumstances (i.e., a biosorbent dosage of 12.0 g/dm3, initial Li concentration of 100 mg/dm3, pH = 5.8, sorption temperature of 25°C, and sorption duration of 6 min). The Freundlich model outperformed the Langmuir model, predicting a maximum sorption capacity of 7.71 mg/g at

25 °C. Using thermodynamic properties established at various isokinetic temperatures, it was discovered that the ion exchange reaction was feasible, spontaneous, and exothermic. A 1.0 M H2SO4 regenerate produced a much higher desorption efficiency and capacity of 97.4 percent and 5.93 mg/g, respectively, during desorption experiments at 25°C when compared to other regenerants (i.e., HCl and NaCl) [43].

In batch tests, the possibility of employing HS to remove Pb^{2+} ions from aqueous solutions by biosorption was explored. Investigations have been done into the effects of initial Pb2+ ions concentration (0.1-1.0 mM), pH (2-9), contact period (10-240 min), and adsorbent amount (0.1-1.0 g). The largest amount of Pb2+ ion adsorption occurred at equilibrium pH = 6.0, which was pH-dependent in all situations. After an equilibrium period of two hours, the HS's equilibrium sorption capabilities were 28.18 mg/g. The experimental results indicated that adsorption, chelation, and ion exchange are the main adsorption mechanisms for binding Pb2+ ion to HS. The adsorption data fit well with the Langmuir isotherm model [44].

Using NaOH aqueous solution and 95% ethanol (SHS), a chemical modification was suggested to boost the maximal sorption capacity of HS for Pb^{2+} ions. Then mercaptoacetic acid was used to modify SHS (MHS) chemically. With a pH greater than 5, MHS's Pb^{2+} ions adsorption reached its maximum. The Langmuir isothermal adsorption model was used to fit the experimental data of Pb^{2+} ions adsorption using MHS, and a maximum adsorption capacity of 61.54 mg/g was achieved [45].

The purpose of the study [46] was to examine if utilizing unmodified HS in ultrasound-assisted adsorption may increase the removal of Pb^{2+} ions from wastewater. Response surface methodology was used to explore and optimize parameters such as contact time, initial Pb^{2+} ions concentration, and wastewater temperature in batch operations. The results showed that even for extremely brief contact times (4–10 min) and for relatively large grounded shell particle sizes, the adsorption effectiveness was high, ranging between 91.6 and 97.3%. (particle size 0.5-0.63 mm). Furthermore, it was shown that the concentration of Pb^{2+} ions at the start of the process is crucial; a larger starting concentration of Pb^{2+} ions corresponded to a higher removal efficiency. The isotherms of ultrasound-assisted adsorption fit the isotherms of Langmuir's model better. The trials at 20 °C resulted in a maximum adsorption capacity of 147 mg/g, demonstrating the excellent adsorption capacity of HS for Pb^{2+} ions [46].

We looked at the batch adsorption of Zn^{2+} ions onto the ground and sieved hazelnut shells. Adsorption's ability to remove Zn^{2+} ions from aqueous solution was tested under a number of conditions, including solution contact time (1-360 minutes), particle size, etc. (75, 75-150, and 150-200 m), solution temperature (25-60 °C), and solution pH. (3–7). In addition, measurements of the zeta potential of particles at various starting pH ranges (2–10) were made. After processing the equilibrium data using the Langmuir and Freundlich isotherm models, greater adsorption capacity values for Zn^{2+} ions were revealed. A pseudo-second-order equation provided the best match when the adsorption kinetics were studied [47].

As can be seen from the above data, the experiments were carried out under different conditions, and the resulting data cannot be correctly compared. The data of studies of various metal ions' adsorption under the same conditions are much more comparable. The source data on HS sorption capacity for 2 or more metal ions are given below.

At pH = 5, in $NaNO_3$ and NaCl ionic media, in the ionic strength range of 0.05-0.5 mol/dm3, the adsorption capacity of HS towards Pb2+ and Cd2+ ions has been investigated. Various kinetic and equilibrium equations were used to fit experimental data, and a statistical analysis was conducted to choose the best model for data fitting. To assess the impact of the ionic medium on the adsorption process, a speciation analysis of the metal ions in solution was also carried out. It was revealed that the largest sorption capacity was for Pb^{2+} ions, the weakest one for Cd^{2+} ions. The Amax value calculated from the Langmuir model in a solution containing 0.1 mol/dm^3 $NaNO_3$ for Pb^{2+} ions was 7.3 mg/g; in a solution containing 0.1 mol/dm^3 NaCl it was 2.8 mg/g. For Cd^{2+} ions, these values were 8.4 and 1.9 mg/g, respectively [48].

Cu^{2+} and Pb^{2+} ions were removed from aqueous solutions using a hazelnut shell-based adsorbent (AHS), which is highly effective, inexpensive, and environmentally friendly. Adsorption kinetics demonstrates that the pseudo-second-order rate model accurately predicts the adsorption rate. The Langmuir model best fits the adsorption isotherm, while the pseudo-second-order rate model accurately depicts the adsorption rate. The maximum Langmuir adsorption capacities for Cu2 + and Pb2+ ions, respectively, were reported to be 21.14 mg/g and 32.74 mg/g [49].

HS and 2 more by-products (spent grain and pecan shells) were studied as a sorption material for removing Cu^{2+} and Zn^{2+} ions from stormwater wastewater under dynamic conditions. Of the three sorbents, HS had the highest sorption coefficient based on Kd ranges of 19,200-106,000 dm^3/kg and 8,610-18,900 dm^3/kg for Zn^{2+} and Cu^{2+} ions, respectively [50].

0.5 g/dm3 of peanut, hazelnut, pistachio, walnut, and almond shells were tested for their ability to remove the necessary amounts of Cd^{2+}, Pb^{2+}, and Hg^{2+} ions from contaminated water. HS was identified as the sorbent with the highest potential and was evaluated in mono- and multi-contaminated mineral water. At the initial concentration of these ions in water, which was 2 μmol/dm^3, the degree of Cd^{2+}, Pb^{2+}, and Hg^{2+} ions removal by HS was 98, 97, and 90%, respectively. For other shells, the removal efficiency was 81-97%, 72-92%, and 65-79%, respectively [51]. The significant potential of this plentiful, inexpensive waste for use in the restoration of contaminated waters is demonstrated by the high efficiencies (>90%) obtained for HS for all elements in ultrapure water as well as for Pb^{2+} and Hg^{2+} ions in mineral water.

Also, Cd^{2+}, Zn^{2+}, Cr(III) ions have been removed from aqueous solutions using HS as a biosorbent substrate. Batch equilibrium studies revealed that pH and surface loading both affected the metal sorption. For Cd^{2+}, Cr(III), and Zn^{2+} ions, the maximum removal was observed only into a specific pH range (at 2.0 mmol/dm^3 metal concentration for Cr(III), Cd^{2+}, and Zn^{2+} ions, pH opt values of 2.4, 2.8, and 3.1, respectively). The metal ion sorption obeyed both the Langmuir and Freundlich isotherms. The values of Amax calculated using the Langmuir equation for Cd^{2+}, Cr(III), and Zn^{2+} ions were 5.42, 3.08, and 1.78 mg/g, respectively [52].

The adsorption behavior of Ni^{2+}, Cd^{2+}, and Pb^{2+} ions from aqueous solutions by HS was investigated. The equilibrium adsorption level was shown to depend on the temperature, concentration, and solution contact duration 120 minutes was discovered to be the equilibrium time. The equilibrium adsorption capacity of HS was determined using the linear Langmuir and Freundlich adsorption isotherms. Thermodynamics' parameters have been determined. The negative values of free change (ΔG) served as evidence for the spontaneous nature of the adsorption of Ni^{2+}, Cd^{2+}, and Pb^{2+} ions onto HS. Additionally, the endothermic character of the adsorption process was revealed by the positive values of enthalpy change (ΔH). The pseudo-second-order kinetic model had the highest correlation coefficients. One of the main adsorption methods for tying divalent metal ions to the HS is probably ion exchange. The selectivity order of the adsorbents is Pb (16.23 mg/g) > Cd (5.42 mg/g) > Ni (3.83 mg/g) [53].

The sorption Cd^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, Cr(III), and Cr(VI) ions are investigated on natural (HS) and modified with citric acid (CHS) and synthetic adsorbents such as cellulose and lignin. In the metal-adsorbent equilibrium studies, the effects of initial metal concentration, pH, temperature, amount of adsorbent, and time on the equilibrium were examined. It was found that the adsorption of Cd^{2+}, Cu^{2+}, Ni^{2+}, Cr(III), and Cr(VI) ions is most accurately described by the Dubinin-Radushkevich model, Co^{2+} and Zn^{2+} ions by the Langmuir model, and Pb^{2+} ions by the Scatchard model. The maximum sorption capacities for the studied native and modified HS ions are given in Table 1.

Table 1. Maximum sorption capacities of native and modified HS for various ions

Ions	**Cd^{2+}**	**Co^{2+}**	**Cr(III)**	**Cr(VI)**	**Cu^{2+}**	**Ni^{2+}**	**Pb^{2+}**	**Zn^{2+}**
HS	7.91	2.18	5.46	8.27	6.67	3.23	28.18	3/99
CHS	46.42	27.88	36.19	22.67	43.46	12.80	99.86	15.49

The calculated thermodynamic parameters of the process indicate that adsorption is mainly a physical and spontaneous process [54].

The effects of pH (1.5-8.0), beginning element concentration (0.5 to 20 mg/dm3), and sorbent dosage (1-20 g/dm3) were examined on the possibility of using HS and SK, wastes from the hazelnut processing facility, for the simultaneous removal of Al^{3+}, Cr(VI), Cu^{2+}, Cd^{2+}, Pb^{2+}, As^{3+} and Fe^{3+} ions from water. The sorbents' precise surface areas were discovered to be 0.676 m^2/g (for HS) and 0.768 m^2/g (for SK). Although pH = 5.0 was shown to be the ideal pH for all elements in both sorbent systems, the amount of heavy metal removed increased as the initial heavy metal concentration grew up to 8 mg/dm3 (except cadmium for HS and copper and cadmium for SK). While 10 g/dm3 was shown to be the ideal sorbent dose for HS, increasing the sorbent dosage decreased the removal percentage for SK. Adsorption models were used to characterize adsorption equilibrium quantitatively, and room-temperature isotherm constants were derived (22 2 C). The majority of the time, the adsorption equilibrium data showed favorable adsorption behavior and fit the Langmuir and Langmuir-Freundlich models well. The maximum sorption capacities for the studied metal ions can be arranged as follows: for HS – Cu^{2+}(10.51 mg/g) > Pb^{2+}(10.26 mg/g) > Al^{3+}(7.75 mg/g) > As^{3+}(7.39 mg/g) > Cr(VI)(7.36 mg/g) > Fe^{3+}(5.47 mg/g) > Cd^{2+}(4.55 mg/g), for SK - Cr(VI)(14.04 mg/g) > As^{3+}(13.0 mg/g) > Pb^{2+}(12.33 mg/g) > Al^{3+}(12.60 mg/g) = Cu^{2+}(12.60 mg/g) > Fe^{3+}(10.50 mg/g) > Cd^{2+}(4.60 mg/g) [55].

3. Use of Hazelnut Processing By-products to Remove Dyes from Aqueous Media

HS has also been studied as a sorption material for removing dyes from aqueous media [56-62]. The relationship between the initial dye concentration, pH, ionic strength, particle size, and temperature was examined with respect to the kinetics of methylene blue (MB) adsorption on the HS. To characterize the rate and transport/kinetic processes of MB adsorption, the first-order Lagergren, pseudo-second-order, mass transfer coefficient, and intraparticle diffusion models were utilized. The pseudo-second-order kinetic model accurately described the kinetic data, according to kinetic studies. The initial adsorption rate significantly increased with increasing temperature, pH, and initial MB concentration. Intraparticle diffusion was shown to be the rate-limiting phase of the adsorption process. Adsorption The activation energy for adsorption was determined to be E = 45.6 kJ/mol.

Additionally, the values of the activation parameters G = 83.4 kJ/mol, H = 1.42.9 kJ/mol, and S = 133.5 J/molK were established [56]. It can be concluded from the experimental results and adsorption models used in this work that the Langmuir isotherm equation accurately reflected equilibrium data. At 25, 35, 45, and 55 degrees Celsius, the highest adsorption capacities of MB were 2.14•104, 2.17•104, 2.20•104, and 2.31•104 mol/g, respectively. The heat of adsorption demonstrated that MB adsorption is endothermic [57, 58].

HS was activated with chemicals (KOH and NaOH) and microwave radiation (MW). Additionally, adsorbents were used to remove MB. The elimination of MB was around 96 percent for NaOH-MW-activated HS and 93 percent for KOH-MW-activated HS, according to the findings. The experimentally determined adsorption capabilities of novel adsorbents were 48 and 47 mg MB/g for NaOH-MW and KOH-MW-activated HS, respectively [59].

Also, MB was removed from the aqueous solution by electrocoagulation with HS adsorption. Optimization of removal efficiency was performed using the response surface method based on a three-variable, three-level Box-Behnken design. Regression analysis revealed a good fit of the experimental data to a second-order polynomial model with an R2 = 0.9534 and an F = 209.88. The maximum removal efficiency of 99.45% was obtained under the following optimal parameters: an adsorbent dosage of 6 g/dm^3, a current density of 2.6 mA/cm^2, and a reaction time of 17.75 min [60].

In addition, HS of various fractions (dp = 125 and 500 µm) was studied for MB and Acid Blue 25 dyes removal under static and dynamic conditions. The maximum sorption capacity calculated on the basis of the Langmuir equation was 76.9 and 60.2 mg/g for MB and Acid Blue 25 for HS fraction with d p = 125 µm and 41.3 and 40.8 mg/g for the fraction with dimensions of 500 µm, respectively. The Langmuir model describes adsorption isotherms. The kinetics of adsorption were explored using Lagergren's model, but a second-order equation provided the best fit. The breakthrough curves were determined by adjusting bed depth, flow rate, and influent concentration during fixed bed adsorption of Methylene Blue on hazelnut shell columns. The data were processed using the Bohart–Adams model and the bed depth service time (BDST) technique was used to estimate column performance [61].

HS was studied as a sorbent for Reactive Red 238 dye removal from simulated solutions under static conditions. It was found that the adsorption isotherm is most accurately described by the Langmuir model (R^2 = 1), and the maximum value of the sorption capacity was 74.53 mg/g. The process kinetics follows the pseudo-second-order model. The mean free energy defined from the Dubinin-Radushkevich equation was found to be 0.077 kJ/mol. All these findings also revealed a favorable physical biosorption [62].

A study was performed to assess the adsorption of Congo Red dye in various concentrations from simulated HS solutions. It was found that HS maximum sorption capacity for the dye was 13.75 mg/g at an initial concentration of 5000 mg/dm3; the contact time was 48 hours. With the initial 500 mg/dm^3 Congo Red solution, HS sorption capacity was 1.87 mg/g [63].

The study aims to remove the textile dyes Disperse Blue 124 from aqueous solutions by using HS under different experimental conditions. The effects of particle size, amount of adsorbents, solution pH, and initial concentration of dyes on adsorption were investigated. The contact time and temperature were kept constant at 30 min and 20 ºC for all sets of experiments. With the initial dye concentration in solutions ranging from $1•10^{-5}$ to $2.5•10^{-4}$ mol/dm^3, the degree of dye removal ranged from 19.9% to 48.0% at pH = 9 [64].

AHS, an HS-based adsorbent modified by 2-acrylamide-2-methyl propane sulfonic acid (AMPS), was created and utilized to adsorb Cu^{2+}, Pb^{2+} ions, MB, and malachite green (MG) dyes from aqueous solutions. According to adsorption kinetics, the Langmuir model offers the best match for the adsorption isotherm and the pseudo-second-order rate model effectively captures the adsorption rate. The maximal Langmuir adsorption capacities for Cu2+ ions, Pb2+ ions, MB, and MG were reported to be 21.14 mg/g, 32.74 mg/g, 68.03 mg/g, and 263.16 mg/g, respectively [65].

In addition to dyes, native HS was studied as a sorbent for the removal of chlorophenols (ortho-, meta- and para) [66] and cypermethrin (antibiotic) [67].

4. The Use of Hazelnut Shell for Activated Carbons Production and as a Sorbent of Pollutants from Aqueous Media

One of HS applications is the production of activated carbons and carbonizates from them and the use of the latter in various productions, including the removal of various pollutants from aqueous media.

One of the applications of various agricultural plant waste and components of wood biomass is the production of activated carbons (AC) [68]. One of the promising precursors for the production of AC is HS due to its high density. HS heat treatment and subsequent chemical and physicochemical treatment can significantly increase sorption performance. Thus, the surface area of the raw HS and the AC obtained by physic-chemical and thermal treatments was measured as 5.92 m^2/g and 1197.6 m^2/g, respectively [69]. In another work [70] AC was prepared in a nitrogen atmosphere at 700 ºC by $ZnCl_2$ activation from HS. BET surface area of AC obtained was determined as 1092 m^2/g.

AC produced from HS at different temperatures using different activators were studied for their ability to remove metal ions, such as Cd^{2+} [71-73], Co^{2+} [73, 74], Cu^{2+} [75-82], Cr(VI) [83], Mn(II) [84], Ni^{2+} [85], Pb^{2+}, from aqueous environments[86-88].

Adsorption of Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+}, the effects of ions found in industrial effluent on the carbon generated by walnut, hazelnut, pistachio, almond, and apricot stone nutshells have been studied. The optimal heating time and temperature for greatest removal efficiency were 15 minutes and 800 degrees Celsius, respectively. The maximum removal was achieved at pH 6–10, 3 mL/min flow rate, and 0.1 g of adsorbent. For HS-based AC, the percentage of metal ion removal was as follows: 90.5% for Cd^{2+}, 92.9% for Cu^2, 96.9% for Pb^{2+}, and 58.8% for Zn^{2+}. Efficiency It also investigated how well carbon worked to remove cations from actual wastewater generated by the copper industries. Findings The results demonstrated that these cations could be significantly removed by the carbon sources mentioned above and that the removal efficiency was much higher in the genuine samples. [89].

HS-based AC was also studied for MB dye removal from simulated solutions. It was found that the maximum MB sorption capacity of the HS-based AC ranged from 204 to 410 mg/g depending on the initial dye concentration and the solution pH [90-93].

Three tetracycline (TC) antibiotics—tetracycline (TC), oxytetracycline (OTC), and chlortetracycline (CTC)—were extracted from aqueous solution using HS HS-derived AC as an adsorbent. Equilibrium was reached after 20 minutes. The order of the AC's greatest adsorption capabilities was OTC (321.5 mg/g), CTC (313.5 mg/g), and TC (302.9 mg/g). The pseudo-second-order kinetic and Langmuir models provided good fits to the data [94].

5. Conclusions

The article summarizes literature data on the use of hazelnut (*Corylus avellana*) shells as a sorption material to remove metal ions, such As^{3+}, Al^{3+}, Cd^{2+}, Co^{2+}, Cr(III) and Cr(VI),

Cu^{2+}, Fe^{3+}, Hg^{2+}, Li^{+}, Ni^{2+}, Pb^{2+}, and Zn^{2+} ions, antibiotics, and dyes from aqueous media. Brief information is provided on the number of hazelnut shells resulting from nut processing, their chemical composition, and methods of reuse. The paper provides the parameters of adsorption processes and the sorption parameters of the studied pollutants. It is shown that the sorption characteristics of crushed hazelnut shells in relation to various pollutants can be improved by chemical modification with various chemicals. It has been determined that the Langmuir model, in most cases, more accurately described the pseudo-second-order model described the pollutants' adsorption isotherms and the process kinetics. It has been shown that hazelnut shells are a good precursor for activated carbon production, effectively removing metal ions, dyes, and antibiotics from aqueous media.

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Conflicts of Interest

The authors declare no conflict of interest.

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