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Pecan Shells and Pecan Shell Activated Carbons as Sorbents to Remove Pollutants from Aqueous Media (a Literature Review)

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Abstract: This review summarizes the literature data on the use of pecan (*Carya illinoinensis*) shells as sorption materials to remove ions of various metals (Cr(III) and Cr(VI), Cu^{2+}, Fe^{3+}, Mn(II), Pb^{2+} and Zn^{2+}), dyes, and some organic compounds from aqueous media. Brief details are given regarding the quantity of pecan shells produced, chemical makeup, physical and chemical characteristics, and methods for reuse in different sectors. The paper provides some adsorption parameters of the pollutants in question. It was found that the Langmuir and Freundlich models, in most cases, accurately describe the pollutant adsorption isotherms, and the processes' kinetics correspond to the pseudo-second-order model. It has been shown that pecan shells are a good precursor for activated carbon production, which can also be used to remove various pollutants from the aquatic medium.

Keywords: pecan nut shells; metal ions; dyes; adsorption; activated carbon.

1. Introduction

Adsorption is currently one of the most efficient strategies to remove different pollutants from polluted natural or improperly treated water. This technique removes pollutants in water with various initial concentrations up to almost zero residual concentrations. However, activated carbons produced from wood or mineral raw materials used for water treatment are expensive, do not always have high sorption capacity, wear out during operation, and require recovery, which contributes to an increase in the cost of water treatment.

The solution is the use of raw lignocellulose materials to process waste and activated carbons based on them as sorbents [1-10]. Of particular interest are waste from processing tree biomass (sawdust, wood chips) and tree fruits (shells, pits, cones, etc.) [11-15]. Another processing waste is the nut shells and the seeds of tree fruit. The latter are formed in huge quantities and can be utilized as sorbents of pollutants or precursors for activated carbons production. Earlier in the review papers, we summarized data on the use of chestnut [16], walnut [17], almond [18], pistachio [19], peach [20], and apricot [21] shells and stones as sorption material to remove pollutants from aqueous media.

One of the widely consumed products is pecan (*Carya illinoinensis*), a woody plant of the walnut family (*Juglandaceae*), distributed mainly in the southern United States, from the southern regions of Iowa and Indiana to Texas and Mississippi inclusive, as well as in Mexico, South Africa, Australia, and Argentina. This deciduous tree reaches 25-40 m in height, with a trunk up to 2-2.5 m in diameter and a tent-shaped crown when growing freely. The bark is thick, deeply cracked, and stratified into plates. False drupes 3-10 in brushes, oblong, tetrahedral, 3.5-8 cm long, dark brown with tufts of brown hairs, with a hard, brittle shell that cracks when ripe almost to the base and often remains on the tree in winter until the nuts fall out. The nut is oblong-ovate or ellipsoidal, almost cylindrical, 2.5-5 cm long, shiny, dark brown with irregular dark brown spots, sometimes tipped at the top, with a brittle shell and a paper-like partition. The seed has a reddish-brown thin shell, with 2 whole cotyledons.

As a nutritious and delicious nut, pecan is rich in crude fat, amino acids, sugars, nitrogen, phosphorus, magnesium, potassium, calcium, and other mineral elements. Its seed kernels are rich in crude fat, amino acids, carbohydrates, nitrogen, phosphorus, magnesium, potassium, calcium, and other mineral elements, phenols, vitamin E, and the content of flavonoids. [22]. Studies have shown that Carya pecan kernels' fat and protein content is mostly higher than that of walnuts and other pecans. The content of phenolic compounds in pecans is higher than that of other nuts and reaches 2,016 mg/100 g. In addition, it is concluded that the pecan is the nut with the highest flavonoid content, reaching 34.01 mg/100 g. Vitamin E content is also higher in pecans than in other nuts (Brazilian chestnuts, hazelnuts, pecans, pine nuts, pistachios, and walnuts) and is 711 mg/kg. Many kinds of finished products can be made into foods, such as nut foods, pecan powder, pecan milk beverages, and pecan crisp candy [22].

As people are increasingly interested in various benefits related to human health, the total production of pecan nuts is on the rise [23]. The production of pecan nuts generates many by-products (pecan green husk and the hard shell). It was estimated that approximately 420,000 tons are produced worldwide every year. These by-products can cause some serious problems, such as water pollution, unpleasant odors, and greenhouse gas emissions. However, these pecan by-products are usually landfilled as garbage, burned, or decomposed in the orchard. Consequently, the efficient use of these pecan by-products would be a strategy that simultaneously helps to preserve the environment and boosts the economic outcome for farmers and companies [23].

The elemental composition of pecan nutshell (PNS), % was determined: C – 53.1, O – 44.7, Ca – 1.8, K – 0.5 [24]. The same source describes the chemical composition of PNS, %: moisture – 6.0, ash – 1.7, cellulose – 32.9, and hemicellulose – 22.5. [25] shows that the moisture content in PNS is 11.5%, ash – 1.76%, crude fiber – 55.65%, carbohydrates – 29.48%, protein – 1.3%, lipids – 0.3 % [26] shows the composition of PNS 16 cultivars grown in Uruguay. It was found that the content of total extractable phenolic compounds was 32.18-116.74 mg GAE/g shell, condensed tannins – 130.03-357.49 mg CE/g shell, anthocyanins – 1.06-3.16 mg of c3g/g shell; antioxidant capacity – 57.15-578.88 mmol Trolox/g kernel. The average extractable phenolic compounds from the PNS of the cultivars evaluated were 2–3 times higher than those found in kernels. The average condensed tannins of the shells (229.00 mg CE/g pecan shell) were also higher than that in the kernels. Total anthocyanin content is considered high if it is referred to as a secondary by-product of the pecan industry. Then PNS could be a good source of natural dyes [26].

The effects of particle size and moisture content on bulk density, particle density, tap density, compressibility, angle of repose, cohesion, angle of internal friction, and flowability were quantified in this study. Equilibrium moisture relations for the shells were also determined at temperatures ranging from 10 to 50°C. The densities (bulk, particle, and tap) significantly decreased, and compressibility significantly increased with particle size and moisture content increased. Increasing the moisture content reduced its flowability from free-flowing (flow index of 15.77) at a moisture content of 4.2% to cohesive (flow index of 3.14) at a moisture content of 24.6%. The cohesive strength of PNS also increased with particle size (0.58 to 1.14 kPa) and moisture content (0.36 to 1.69 kPa). An average angle of internal friction of 41.28° was obtained and was not significantly affected by moisture content and particle size. The angles of repose of pecan shells varied from 33.1 degrees to 46.3 degrees. The equilibrium moisture relation curves for the shells were sigmoidal in shape and showed that PNS should be stored at moisture contents of less than 18.03% to minimize microbial activity. The modified Henderson equation best predicted the equilibrium moisture relation curves [27].

Also, PNS were characterized by morphological, chemical, and thermal analysis. Degradation kinetics was performed using the Flynn-Wall-Ozawa and Criado methods. PNS thermal degradation starts at 250°C and takes place in three steps. PNS activation energy ranges from 156.25 kJ/mol to 264.21 kJ/mol. The degradation is governed by diffusion until a conversion value of 0.5 is reached, and when it is higher, multiple degradation mechanisms take place. It is not possible to determine which one has taken place. PNS matrices require a processing temperature below 220°C [28]. The thermal decomposition process was composed of four stages: moisture evaporation, hemicellulose decomposition, cellulose decomposition, and lignin degradation. The peak temperatures for hemicelluloses (275 to 315°C) and cellulose (348 to 385°C) degradation increased with the heating rate. The amount of energy required to degrade pecan shells thermally was about 30% of the energy content of the PNS [29].

Considering the chemical composition of PNS, it has been shown that lignin and holocellulose [30], polyphenols such as catechin, epicatechin, (epi)gallocatechin, epicatechin gallate, (epi)gallocatechin gallate and (epi)afzelecin [31], flavonoids [32], proanthocyanidins [33] can be recovered and produced from it. Extracts from PNS also have high antioxidant activity [34-36]. PNS extracts are being suggested for usage in packaging materials [37]. Crushed PNS can be used as a bio-filler in lactic acid-based biodegradable composite materials [38], as a functional ingredient in bread and wheat tortillas [39], and for silver nanoparticle recovery [40]. PNS is also used as a smoke flavor for smoking chickens [41-43].

One of PNS applications is water treatment sorption material to remove various pollutants from water.

2. Using Pecan Nut Shell to Remove Metal Ions from Aqueous Media

There are a number of publications on the use of PNS for various metal ion removal from aqueous media. Thus, in particular, there is a study on the removal of Cr(VI) ions from simulated PNS solutions of two grades with fractions of 0.42 mm and 0.85 mm at pH = 2.5 and 6.18 under dynamic conditions. It was revealed that along with Cr(VI) ion sorption, the latter is reduced to Cr(III) ions with subsequent adsorption. It is found that the Thomas model adequately describes the adsorption isotherm. It was found that the maximum chromium ions removal degree is achieved at pH = 2.5 and PNS particle size up to 0.42 mm [44].

Adsorption of Pb^{2+} ions by PNS under static conditions was also studied. It was found that the adsorption isotherm is well described by the Redlich–Peterson model; the maximum sorption capacity for lead ions was 5.94 mg/g at pH = 5, and the PNS dosage was 8 mg/g [45].

Reported for the feasibility of PNS as an alternative biosorbent to remove Cr(III), Fe^{3+}, and Zn^{2+} ions from aqueous solutions. The ability of PNS to remove these metallic ions was investigated by using a batch biosorption procedure. The effects, such as pH and the biosorbent dosage, on the adsorption capacities of PNS were studied. The adsorption kinetics is the one that fits the fractional-order kinetic model better. Taking into account a statistical error function, the data were best fitted to Sips isotherm models. The maximum biosorption capacity of PNS were 93.01, 76.59, and 107.9 mg/g for Cr(III), Fe^{3+}, and Zn^{2+} ions, respectively [46].

Also, PNS was studied as a biosorbent to remove Cu^{2+}, Mn(II), and Pb^{2+} ions from aqueous solutions. The effects of pH biosorbent dosage on the adsorption capacities of PNS were studied. Four kinetic models were tested, and the adsorption kinetics better fitted to the fractional-order kinetic model. Besides that, the kinetic data were also fitted to the intra-particle diffusion model, presenting three linear regions, indicating that the kinetics of adsorption should follow multiple sorption rates. The data best fit the Sips isotherm model. The maximum biosorption capacities of PNS were 1.35, 1.78, and 0.946 mmol/g for Cu^{2+}, Mn(II) and Pb^{2+}, respectively [47].

3. Using Pecan Nut Shell to Remove Dyes from Aqueous Media

There are several publications on the use of PNS for the removal of dyes from aqueous media. Thus, a biosorbent was prepared from PNS and HCl in order to treat colored effluents containing the dye Methyl violet 2B (MV2B) using batch and fixed-bed operation modes. The best pH for MV2B biosorption on the PNS was pH = 8.5. The kinetic profile was better described by the general order model, being the equilibrium rapidly reached in the first 5 min for different initial concentrations MV2B. The Langmuir model better described the equilibrium curves, indicating homogenous biosorption. The maximum biosorption capacity of 642 mg/g was reached at 328 K. Biosorption was favorable and endothermic. PPP has removed 94.1% of color in the simulated effluent. The fixed-bed assays revealed that the column packed with PPP could operate during 52.5 h with a height of 25 cm. The Thomas, Bohart-Adams, and Yoon-Nelson models were suitable to describe the dynamic curves [48].

PNS was also studied to determine the ability to remove acid blue 25 dye from simulated solutions under static conditions. It was determined that the maximum sorption capacity of 10.77 mg/g is provided by a sorbent dosage of 8 g/dm^3 and pH = 5. It was found that the Redlich–Peterson model gave a better fit for modeling the adsorption isotherms because this model provides a better behavior of the residuals, and suitable values of R^2 are obtained in most of the correlations performed [45].

Biomass from PNS was employed to study the adsorption mechanism of a relevant textile pollutant, crystal violet (CV). The adsorption energy was calculated, and the adsorption mechanism was analyzed, thus suggesting that hydrogen bindings and van der Waals interactions could be possible for the adsorption of this dye on PNS at optimum pH =2. The energy for the adsorption of CV on PNS was 13.18 kJ/mol at low temperature (298 K) and 13.22 kJ/mol at high temperature (328 K) [49].

The biomass-derived PNS were used as a biosorbent of acid blue 74 (AB74), acid blue 25 (AB25), and reactive blue 4 (RB4) dyes. Results suggest that the calcium compounds occurring in pecan shells are responsible for the favorable adsorption of anionic dyes, specifically for removing AB74. Biosorption results showed that pecan shell is a more suitable adsorbent in dye removal processes using batch configuration rather than packed-bed columns [50].

4. The Use of Pecan Nut Shells to Produce Activated Carbons and the Use of the Latter to Treat Aqueous Media to Remove Various Pollutants

As seen from the above, there are few reports in the world literature about using native or chemically treated PNS to remove metal ions and dyes from aqueous media. There is much more information about the use of PNS as a precursor for the production of activated carbons (AC) or carbonates and the use of the latter to remove various pollutants from aqueous media. It is shown that AC from PNS can be produced by raw materials pyrolysis in an air atmosphere at 300-600°C [51, 52], heating by microwaves [53, 54], and other methods. To increase the surface, various activators are used, such as H_3PO_4 [55], CO_2 [56], $ZnCl_2$, KOH, NaOH, and H_2SO_4 [57]. The characterization results demonstrated that the development of pore structure was apparent at temperatures ⩾250°C and reached 1130 m^2/g surface area and 0.34 cm^3/g pore volume, respectively, at 500°C [58]. It was determined that the surface area of the AC produced from PNS activated with phosphoric acid can exceed 1,500 m^2/g [56]. The spectra of ^{1}H, ^{13}C, and ^{31}P of the electron paramagnetic resonance of AC produced from pecan shells activated with phosphoric acid and charred at 450°C for 4 hours with different air flow rates are given in [59]. Several structural parameters were calculated, such as the molar fraction of bridged aromatic carbons, the number of carbon atoms in the aromatic ring, and the number of phenolic carbon atoms in the aromatic ring system. Economic calculations showed that pecan nutshell AC cost was 2.89 $/kg in 2003 [60].

4.1. Using pecan shell-activated carbons to remove metal ions from aqueous media.

AC from PNS were studied as sorbents to remove ions of various metals from aqueous media. Thus, in particular, ehe pyrolysis process was used to produce biochar and carried out a study to remove Cr(VI) ions in aqueous solutions. The maximum removal reached was 94 % for a Cr(VI) solution at 50 mg L^{-1}. The Elovich model described the adsorption kinetics of Cr(VI) on the biochar very well, and the Sips model described the adsorption equilibrium. The thermodynamic parameters showed that this adsorption process was spontaneous, favorable, and exothermic [61].

AC produced at 215-500°C was used to remove Cu^{2+} ions from aqueous media. Air and phosphoric acid are used for the oxidation and the modification or development of oxygen- or phosphorus/ oxygen-containing groups on the carbon surface. Besides, it was noted that a temperature increase from 215°C to 500°C results in an AC surface area increase from 27 m^2/g to 1017 m^2/g. The adsorption capacity of the produced carbon was significantly higher than that of the commercial AC tested and comparable to an ion exchange resin designed for Cu^{2+} ions adsorption [56, 62]. The commercial GACs exhibited the lowest number of titratable functional groups and among the lowest Cu^{2+} ion adsorption values [56]. It was determined that AC from PNS activated with phosphoric acid had sorption capacities 0.97 and 1.3 mmol of Cu^{2+} ions per gram of AC when the carbon had been in contact with a Cu^{2+} solution with the initial concentration of 10 and 20 mM of Cu^{2+} ions, respectively [63].

PNS-based activated carbon (PNSAC) had a high specific surface area (1500 m^2/g) and pore volume (0.7 cm^3/g). The maximum adsorption capacity of the PNSAC was found to be 41.66 mg/g at 55 mg/dm^3 of Fe^{2+} ions at pH = 3 and 3 g/dm^3 adsorbent dose, at 90 min and 30°C. The pseudo-second-order model can best describe Fe^{2+} ion adsorption. The adsorption system was thermodynamically favorable, endothermic, and increased in entropy. The experimental data were fitted against common adsorption isotherms and yielded excellent fits in the following order: Temkin > Freundlich > Sips > Halsey Dubinin–Radushkevich > Langmuir > Harkins–Jura > Redlich–Peterson [64].

In addition, PNS was exposed to microwave radiation at various capacities and times. The resulting AC was used to remove Pb^{2+} ions from simulated solutions. It was found that the highest Pb^{2+} ions removal of 80.3 mg/g was achieved at the highest energy input of 11.7 kJ/g [65].

Also, PNSAC was prepared, characterized, and applied to remove Ba^{2+} and Sr^{2+} ions from synthetic fracking wastewater. The PNSAC had a high specific surface area of 1517 m^2/g and a pore volume of 0.8 cm^3/g. Results showed that the Langmuir model best fits the adsorption system, with the PNSAC having a maximum adsorptive capacity of 3.33 mg/g for Ba^{2+} and 8.8 mg/g for Sr^{2+} ions. Pseudo-second order kinetic model had the best fit, indicating chemisorption as the rate-limiting step. Kinetic studies revealed that sorption was not limited by intraparticle diffusion for both metals. The adsorption process was thermodynamically favorable and endothermic [66].

A study was conducted on the removal of Cu^{2+}, Pb^{2+}, and Zn^{2+} ions from potable water using PNSAC. It was found that either steam-activated PNS removed nearly 100% of Pb^{2+} ions, 90-95% of Cu^{2+} ions, and 80-90% of Zn^{2+} ions [67]. PNS was activated by phosphoric acid, steam, or carbon dioxide activation methods. The results obtained from this study showed that acid-activated PNSAC adsorbed more Pb^{2+} ions and Zn^{2+} ions than any of the other carbons, especially at carbon doses of 0.2–1.0%. However, steam-activated PNSAC adsorbed more Cu^{2+} ions than the other carbons, particularly using carbon doses above 0.2% [68].

PNSAC has also been assessed and compared in removing Cd^{2+}, Cu^{2+}, Ni^{2+}, and Zn^{2+} ions, giving special emphasis to the analysis of competitive adsorption of these pollutants in binary systems. Results showed that a synthesis route combining physical and chemical activation substantially improved these adsorbents' adsorption properties. Chemical activation may improve metal adsorption using these adsorbents by up to 12-14 %, where adsorption capacities ranged from 0.011 to 0.368 mmol/g [69].

The adsorption of heavy metals on AC derived from *Carya illinoinensis* biomass was studied using molecular simulation tools to understand the adsorption mechanism. Particularly, it was possible to obtain samples of biochar that were very efficient for the removal of Al^{3+}, Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} ions from water, using relatively low temperatures of carbonization (200–350°C) and low processing times (20–50 min). The most influencing factor in the final properties of biochar was the maximum temperature of the thermal treatment. The biochars obtained were rich in oxygen functional groups (carboxylic and phenolic), which favored the removal of heavy metals from water by complexation and ionic exchange mechanisms [70].

Carbons loaded with specific chemical moieties were prepared from PNS employing a natural modifier agent obtained from eggshell, which is rich in calcium, for the selective fluoride adsorption from water. Fluoride adsorption experiments were performed in synthetic and real groundwater samples. Results showed that PNSAC modified with a calcium solution extracted from egg shells was more effective for fluoride removal than those using the nutshell precursor. The calcium chemical species on the carbon surfaces were more important in the fluoride adsorption process than the carbon textural parameters [71].

4.2. Using pecan shell-activated carbons to remove dyes and other organic compounds from aqueous media.

There are several publications in the world literature on removing dyes from aqueous media by AC produced from PNS. In particular, on the adsorption of the Methylene blue dye by PNSAC under static conditions at temperatures 15-45°C. The maximum sorption capacity at these temperatures was found to fall within the range of 106.61 to 118.42 mg/g. It was found that adsorption isotherms are well described by the Langmuir model [72]. It is noted that PNSACs have large surface areas (2,342 m^2/g) and, correspondingly, high values of maximum sorption capacity (1,190 mg/g) [73]. The kinetic experimental data better correlated with the pseudo-second-order kinetic and Elovich equations, and the Langmuir model showed a better fit for the data of MB adsorption. In addition, the thermodynamic data suggested a spontaneous adsorption process with endothermic characteristics [73]. [74] shows that the maximum sorption capacity of PNSAC resulting from phosphoric acid activation for Methylene blue is 400 mg/g.

PNSAC was prepared for removing Reactive Red 141 from aqueous solutions. The biochar presented a micro/mesoporous structure with a surface area of 93 m^2/g, considered high for biomass-derived materials. For both raw PNS and PNSAC, the Reactive Red 141 dye adsorption was favored under acid conditions (pH of 2 and 3, respectively). The dye removal percentage was 85% using PNSAC and was only 23% when raw PNS was used. The adsorption kinetics dye on the biochar followed the pseudo-second-order model. The Freundlich model represented the equilibrium isotherms well. The maximum adsorption capacity was approx. 130 mg/g. The adsorption was spontaneous, favorable, and exothermic ($\Delta H^0 = -56.42$ kJ/mol) [75].

PNSAC with ZnO (biochar-ZnO) was prepared to obtain a potential catalyst for Reactive Red 97 dye degradation from aqueous solutions. The composites presented higher activity compared to ZnO pure. The composite with a greater amount of ZnO supported in the biochar (N20Z) degraded 100 % of the dye in only 67 min (30 min biosorption + 37 min photocatalysis). The recycling of the composite N20Z indicated that it could be used for more than 9 cycles and be easily removed from the solution. Radical scavenger tests indicated that •OH and h+ were the predominant active species involved in the degradation of Reactive Red 97 [76].

Also, four methods to prepare activated carbon using pecan nut shells, an agricultural waste, as an alternative precursor instead of conventional materials such as coconut shells or wood. The preparation methods were carbonization (PNSAC), carbonization/water activation (PNSAC-H_2O), carbonization/microwave treatment (PNSAC-MW), and carbonization/activation/microwave treatment (PNSAC-H_2O-MW). The sorption equilibrium time for the tartrazine dye sorption was determined. The prepared AC that presented the best sorption capacity was PNSAC-H_2O (8.2 mg/g) and PNSAC-MW (5.1 mg/g); both materials' sorption equilibrium time was 24 h. The sorption experiments showed a good fit for the pseudo-second-order equation and the Freundlich mode [77].

The removal of tartrazine (Acid yellow 23) dye onto PNSAC was obtained under specific conditions and one one-step simultaneous carbonization/activation process. Batch adsorption studies were performed for the removal of tartrazine azoic dye from aqueous solutions by two materials obtained at 600°C (PNSAC-600) and 857°C (PNSAC-857) and another two materials prepared at the same temperatures but simultaneously activated with steam (PNSAC-600-H_2O and PNSAC-857-H_2O). The maximum adsorption occurred when AC was steam activated and was 4.47 and 13.66 mg/g for NAC-600-H_2O and NAC-857-H_2O, respectively. The results showed that the adsorption of tartrazine onto carbonaceous materials from PNS best fit the pseudo-second-order model, and the rate constants ranged from 489.3 to 509.4 g/mg•h [78]. It was found that the Langmuir-Freundlich equilibrium isotherm model provides the best fit with the experimental data [79].

PNSAC was also studied for the ability to remove the Tartrazine and Allura Red dyes individually or in a mixture in a 50:50 ratio. It was found that at an initial dye concentration of 10 mg/dm^3, the degree of removal of both dyes was 95%, and in the case of a mixture of dyes, it was 50% removal. The sorption process data showed an acceptable fit to the Freundlich kinetic model [80].

Also, PNSACs produced by activation of various compounds (steam, H_3PO_4, and CO_2) were studied to determine the ability to remove the Atrazine and Metolachlor herbicides from aqueous solutions. PNSAC's maximum sorption capacity for Atrazine was found to be 32.2, 30.0, and 9.0 mcg/g AC, respectively. PNSACs were found to be more efficient at removing Atrazine from water than commercial ACs. It was also revealed that removing metolachlor by PNSAC produced by steam activation or using H_3PO_4 showed the best values of the maximum sorption capacity (66.7 and 62.0 μg/g, respectively) [81].

AC produced from pecan, almonds, and walnut shells removed chlorination products such as bromodichloromethane, bromoform, and dibromochloromethane from potable water under dynamic conditions. The results indicate that only two of the eight ACs failed to remove the above-chlorinated hydrocarbons more than the commercial ACs. In both cases, these filters contained carbons with either 100% acid-activated almond shells or 100% acid-activated PNS. All six other filters contained carbons with either 50% or 100% steam-activated PNS or steam-activated walnut shells [82].

Также определялась the effectiveness of using pecan and almond shell-based granular AC (GACs) in the adsorption of volatile organic compounds (VOCs) (bromo-dichloromethane, benzene, carbon tetrachloride, 1,1,1-trichloromethane, chloroform, and 1,1-dichloromethane) compared to the adsorption efficiency of commercially used AC. The PNS-based GACs were activated using steam, CO_2, or phosphoric acid. An almond shell-based GAC was activated with phosphoric acid. The steam-activated PNSAC adsorbed more total VOCs than the other experimental AC. PNS, steam-activated, and acid-activated GACs showed higher adsorption of 1,1,1-trichloroethane than the other carbons studied [83].

Also, the adsorption efficiency of granular PNSAC will be compared with the adsorption efficiency of the commercial AC Filtrasorb 200 with respect to the uptake of the organic components responsible for the chemical oxygen demand (COD) of municipal wastewater. The results indicate that steam-activated and acid-activated PNSAC had higher adsorption for organic matter measured as COD, than carbon dioxide-activated PNSAC or Filtrasorb 200 at all the AC dosages used during the experiment. The higher adsorption may be related to surface area, as the two ACs with the highest surface area also had the highest organic matter adsorption [84, 85].

5. Conclusions

As can be seen, this review summarizes the literature data on the use of pecan (*Carya illinoinensis*) shells as sorption materials to remove ions of various metals (Cr(III) and Cr(VI), Cu^{2+}, Fe^{3+}, Mn(II), Pb^{2+} and Zn^{2+}), dyes, and some organic compounds from aqueous medium. The paper provides brief information on the amount of pecan shells generated, their chemical composition, physico-chemical properties, and recycling applications in various industries. The paper provides some adsorption parameters of the pollutants in question. It was found that the Langmuir and Freundlich models, in most cases, accurately present the pollutant adsorption isotherms, and the kinetics of the processes correspond to the pseudo-second-order model. It was shown that pecan shells are a good precursor for activated carbon production, which can also be used to remove various pollutants (metal ions, dyes, pesticides, chlorinated hydrocarbons) from aquatic environments.

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Conflicts of Interest

The authors declare no conflict of interest.

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