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Removal of Various Pollutants from Aquatic Environments with Cashew Processing Waste (a Literature Review)

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Abstract: The paper summarizes literature data on the use of Cashew nut shells as a sorption material to remove metal ions ($Cd^{2+,}$ Co^{2+}, Cr(III), Cr(VI), Cu^{2+}, Mn(II), Ni^{2+}, Pb^{2+}, Zn^{2+}), dyes, and phenol from simulated and wastewater. It provides brief information on the amount of Cashew nut shell generated, its chemical composition, and its methods used in various industries as a secondary raw material. The paper presents the Cashew nut shell adsorption process parameters for the pollutants. It is shown that Cashew nut shell treatment with various chemicals improves sorption characteristics for various pollutants. It was found that adsorption isotherms are described by various models, most often by those of Langmuir and Freundlich. In most cases, the process kinetics follows the pseudo-second-order model. It is also shown that Cashew nutshell is a good precursor for activated carbons and carbonizates production, which is also used to remove organic and inorganic pollutants from aquatic environments.

Keywords: cashew nut shell; metal and metalloid ions; dyes; phenol; removal; adsorption models; process kinetics.

1. Introduction

Today, the global community is becoming increasingly concerned about the pollution of natural water bodies by various pollutants [1]. The source of chemicals that ingress into water is the wastewater from various industrial enterprises. There are many methods to remove pollutants (mechanical, physico-chemical, chemical, and biological) from wastewater [2]. Adsorption takes a dominant position among wastewater treatment methods since it allows the extraction of pollutants of various initial concentrations up to almost complete removal of the pollutant [3].

However, activated carbons (AC) used on an industrial scale have several disadvantages, such as high cost, the need for recovery, poor sorption characteristics for some pollutants (e.g., metal ions), the low mechanical strength of granules, etc. All this increases treatment costs, affecting the final product cost [4].

Given the above, an innovative environmental protection trend is being intensively developed in the world community – using cheap, efficient, multi-tonnage agricultural waste as reagents to remove pollutants from water environments [5-14].

Wood biomass components, such as leaves [15-19], needles [19, 20], bark [21-23], cones [24, 25], acorns [26, 27], etc., are of particular interest as sorption materials (SM). Processing tree fruits results in various types of waste, such as peel [28-31], pits, and shells of fruits [32-38]. The latter are formed in mass, do not rot for a long time due to their dense texture, and take up a lot of space for storage near processing plants. We have shown in several reviews that the shells and pits of tree fruits are a valuable source of chemical compounds, a component of various materials, and an effective SM for removing various chemicals from aqueous media [34-38].

This review summarizes data about using cashew nut shells as an SM to remove various pollutants from aqueous media.

Cashew or *Anacardium occidentale* is a small 10-12m high evergreen tree with a short, often irregularly shaped trunk. The crown is wide-spreading; its diameter is comparable to the tree's height and is 8-10m. The leaves are alternate, leathery textured, elliptic to obovate, with smooth margins, 4-22cm long and 2-15cm wide. The flowers are pale green, then turning reddish, with five slender, acute petals 7-15mm long, arranged in a panicle or corymb up to 26cm long. What is often called cashew fruits or “cashew apples” is an overgrown juicy pedicel, or, more correctly, a receptacle (floral disk). They are yellow or red, 5-11cm long, and have a pear or diamond oblong shape. Hidden under the skin is a yellow fibrous, very juicy, slightly astringent, sour-tasting pulp. Botanists refer to such formations as “accessory fruit”. The true cashew fruit develops at the very end of the pedicel, following the apple accessory fruit. This is a nut resembling miniature boxing gloves covered with a double shell. The outer one is green and smooth and contains caustic phenolic resin. The inner one looks like a dense shell covered with honeycomb-like cells, with an edible nut kernel inside, similar to a human kidney. The average weight of one nut is 1.5g [39].

Cashew is primarily grown in Asia (India, Philippines, Vietnam, Thailand, Indonesia, Malaysia, and Sri Lanka), South America (Brazil, Costa Rica, Columbia, Honduras, and El Salvador), Africa (Nigeria, Cote d’Ivoire, Tanzania, Mozambique, Senegal, Ghana, and Madagascar) and Oceania (Philippines, Indonesia) [40]. The main suppliers of cashew nuts to the world market in 2020 were Cote d’Ivoire (849 thousand tons), India (773 thousand tons), Vietnam (349 thousand tons), Burundi (301 thousand tons) and the Philippines (256 thousand tons) [41]. In total, 4181 thousand tons of cashew nuts were harvested globally in 2020 [41].

It is determined that the weight of the cashew kernel averages 35-45% of the nut weight; consequently, the weight of the shell is 55-65%.

The whole cashew nut is rich in healthy fatty acids, physiologically active amino acids, selenium, phytosterols, tocopherols, high levels of starch, alkyl-phenols, and a polysaccharide profile that is crucial for both industrial and dietary purposes [40].

Cashew nuts contain dry matter – 98.18%, moisture – 1.82%, ash – 3.23%, fiber – 6.43%, protein – 20.51%, fat – 47.67%, carbohydrate – 22.16%, energy value – 528.15 Kcal/100g, Fe - 0.69mg/100g DM, Mg - 10.79mg/100g DM [42].

The chemical composition of cashew nut shell (CNS) was also determined: crude fiber – 23.05%, neutral detergent fiber – 26.30%, acid detergent fiber – 18.95%, acid detergent liquid – 7.45%, cellulose – 11.50%, hemicellulose – 7.35%, volatile matter – 65.21%, moisture –

9.83%, ash – 2.75% [39, 40]. The elemental composition of CNS was also determined: carbon – 45.21%, hydrogen – 4.25%, oxygen – 37.75%, nitrogen – 0.21%, and sulfur – not found [40]. The content of vitamins in CNS was found to be mg/100g: A - 8.12, B – 4.27, B2 – 7.25, B6 – 0.64, C – 46.41, D – 0.27, E – 0.46, K – 0.62 [43, 44].

Cashew nut processing products are utilized in various goods, including adhesive resins, bio-ethanol, biodiesel, surface coating agents, dyes, pesticides, larvicides, anti-termite, rubber, and pyrotechnic [45-54]. In addition, dark reddish-brown liquid, often known as cashew nut shell liquid (CNSL), is extracted from nut shells, making up 15-30% of the honeycomb structure of cashew nut shells. CNSL is widely used in industry to produce various chemical compounds such as anacardic acid, 2-methyl cardol, cardanol, and cardol. The composition of CNSL differs depending on the method of extraction. Natural CNSL, which is extracted by using cold solvents or mechanical extraction, contains anacardic acid (60–65%), cardanol (10–15%), cardol (20%), and traces of 2-methylcardol. On the other hand, technical cashew nut shell liquid is extracted by roasting the cashew nuts at higher temperatures, causing decarboxylation of most anacardic acid to cardanol as a major component (60–65%). Other CNSL components include cardol (15–20%), polymeric materials (10%), and traces of 2-methylcardol. CNSL is also used, in particular, for synthesizing corrosion inhibitors [55], adhesive compositions [56], polyurethanes [57], and many other materials. However, this topic is not the main one for this review. More detailed information about the SNSL composition and other applications is given in [58, 59].

One of CNS applications is to use them as a sorption material (either in native or modified form) to remove various pollutants from aqueous media.

2. The use of cashew nut shells to remove heavy metal ions from aqueous media

As shown above, CNS composition includes a variety of biologically active compounds and vitamins containing various functional groupings. In addition, the presence of a large amount of oxygen was revealed in the composition of various oxygen-containing functional groups. This is prone to high sorption characteristics for heavy metal ions.

This chapter summarizes data on removing metal ions by CNS from aqueous media. The material is given as an alphabetical list of metal ions for ease of perception.

2.1. Cd(II) ions.

So, in particular, CNS has been used to remove Cd^{2+} from an aquatic solution. It was initially determined that the BET surface area, pore volume, average pore diameter, and bulk density of the CNS were 395m^2/g, 0.4732cm^3/g, 5.89nm, and 0.415g/cm^3, respectively. The maximum of Cd^{2+} ions adsorption was obtained at pH~5.0. The monolayer adsorption capacity was found to be 22.11mg/g. The adsorption of the Cd^{2+} ion on CNS reached equilibrium in 30 min. The two-parameter and three-parameter isotherm models, Langmuir, Freundlich, Redlich-Peterson, Koble-Corrigan, Toth, and Sips isotherm models best describe the adsorption of Cd^{2+} ion onto CNS. The kinetic data at 30-60°C showed that the pseudo-second-order kinetic model was obeyed better than the pseudo-first-order, Elovich kinetic, and intraparticle diffusion models, which indicates that chemisorption is the rate-limiting step [60].

2.2. Cu(II) ions.

The effect of various parameters such as solution pH, CNS dose, contact time, and initial Cu^{2+} ions concentration on adsorption efficiency were examined. The Cu^{2+} ions adsorption was favored with a maximum adsorption at pH~5.0, CNS dose 3g/dm^3, contact time 30 min, and initial Cu^{2+} ion concentration 20mg/dm^3, respectively. The experimental data were analyzed by Langmuir, Freundlich, Redlich-Peterson, Dubinin-Radushkevich, Koble-Corrigan, Sips, Toth, and Temkin adsorption isotherms. It was determined that the adsorption isotherm is most accurately described by the Koble-Corrigan model [61]. It was shown that the pseudo-second second-order kinetic model could describe the adsorption of Cu^{2+}. The thermodynamic calculations indicated the feasibility, exothermic, and spontaneous nature of the adsorption of Cu^{2+} ions onto CNS at 30-60°C [62].

Also, the synthesis and characterization of nano-scale zero-valent-impregnated CNS (NZVI-CNS) was studied to remove Cu ions. The adsorption parameters such as solution pH, adsorbent dose, initial copper ions concentration, contact time, and temperature were optimized. The adsorption experimental data were best fitted with the pseudo-second-order and Freundlich models. The thermodynamic studies showed that the adsorption process was spontaneous, feasible, and exothermic [63].

2.3. Ni(II) ions.

The adsorption behavior of Ni^{2+} ions from aqueous solution onto CNS was investigated as a function of parameters. The equilibrium data fits well for both Langmuir and Freundlich adsorption isotherms. The Langmuir monolayer adsorption capacity of CNS was found to be 18.868mg/g. Thermodynamic parameters have also been evaluated, and it has been found that the sorption process was feasible, spontaneous, and exothermic. The result of the kinetic study shows that the adsorption of Ni^{2+} ions could be described by the pseudo-second-order equation. The adsorption process was found to be controlled by both surface and pore diffusion, with surface diffusion at the earlier stages followed by pore diffusion at the later stages. Analysis of adsorption data using a Boyd kinetic plot confirmed that external mass transfer is the rate-determining step in the sorption process [64].

The NZVI-CNS was successfully synthesized through the impregnated method, which been effectively used to remove Ni^{2+} ions from the aqueous solution. The results showed that adsorption followed the pseudo-first-order model based on a higher correlation coefficient with low error values. The maximum monolayer adsorption capacity for the removal of Ni^{2+} ions was found to be 70.05mg/g at an optimum condition. Among these, the Freundlich isotherm model was identified as a well-suitable adsorption isotherm model. The values of thermodynamic parameters such as Gibbs free energy, entropy, and enthalpy indicated that the adsorption process was spontaneous, feasible, and exothermic [65].

2.4. Pb(II) ions.

Adsorption of Pb^{2+} ions by CNS under static conditions was studied. Isotherms are constructed for various initial concentrations of Pb^{2+} ions in solution. It was determined that at an initial concentration of 10mg/dm^3, the maximum sorption capacity was 0.27mg/g, and at 50mg/dm^3 – 1.38mg/g. It was found that the Langmuir model most accurately describes the

adsorption isotherms, and the kinetics of the process follows the pseudo-second-order model [66].

Another study revealed that the maximum sorption capacity of CNS for the Pb^{2+} ions is 17.82mg/g. The equilibrium data fit well in the Freundlich isotherm, which confirmed the multilayer coverage of Pb^{2+} ions onto CNS. The kinetics of Pb^{2+} ion adsorption by CNS is better described by the pseudo-second-order equation. Various thermodynamic parameters, such as ΔG, ΔH, and ΔS, have also been evaluated, and it has been found that the adsorption process was feasible, spontaneous, and exothermic [67].

CNS was modified with various chemicals to increase the sorption characteristics of CNS for the Pb^{2+} ions. Thus, CNS treatment with a sulfuric acid solution (STCNS) significantly increased sorption characteristics. The maximum adsorption capacity of Pb^{2+} ions on STCNS was determined as 408.6, 432, 446.3, and 480.5mg/g, respectively, at different temperatures (30, 40, 50, and 60°C). It was found that the Freundlich isotherm model fits best with the experimental data at different temperatures studied. The thermodynamic parameters (ΔG°, ΔH°, and ΔS°) were calculated, and the thermodynamic properties of Pb^{2+} ions-STCNS system indicate the exothermic process. The adsorption results clearly showed that the adsorption of Pb^{2+} ions onto STCNS followed a pseudo-second-order model, and the adsorption was both by film diffusion and intraparticle diffusion [68]. The results showed that STCNS exhibited the highest adsorption capacity. The chemical treatment removes impurities, alters the surface functional groups, and significantly improves specific surface areas and pore volumes of native CNS. Surface adsorption and intra-particle diffusion steps were found to substantially affect the overall adsorption process of Pb^{2+} on STCNS [69].

Modified CNSL was also used for the adsorption of Pb^{2+} ions. A range of thiol-silica composites were prepared using CNSL or one of its phenolic constituents, cardanol, as templates. The procedure involved the formation of a CNSL or cardanol emulsion in a water-ethanol system into which (3-mercaptopropyl)-trimethoxysilane and tetraethyl orthosilicate were simultaneously added at various ratios. Results indicated that the thiol-silica composites were successfully prepared, with thiol group loadings ranging from 1.6-2.5mmol/g. The materials were tested for Pb^{2+} adsorption, and results showed that they had maximum adsorption capacities up to 66.7mg/g, depending on the thiol group loading and type of template used in preparing the adsorbent [70].

2.5. Zn(II) ions.

CNS was investigated for the removal of Zn^{2+} from an aqueous environment. The equilibrium data fit well with the Langmuir isotherm and pseudo-second-order kinetic models. Langmuir monolayer adsorption capacity of CNS was examined as 24.98mg/g. Changes in standard ΔG°, ΔH°, and ΔS° showed that the sorption of Zn^{2+} ions onto CNS is spontaneous and exothermic at 303–333K. Effective diffusivity values were found to be $1.927 \cdot 10^{-11}$ ($10mg/dm^3$) and $2.362 \cdot 10^{-11}$ ($50mg/dm^3$)m^2/s [71].

Also, Zn^{2+} ions from the aqueous solution were removed using NZVI-CNS. Adsorption kinetic data followed the pseudo-first-order kinetic model. Moreover, the equilibrium adsorption data were best fitted with a Freundlich model. Langmuir monolayer adsorption capacity was calculated as 94.46mg of Zn^{2+} ions/g of NZVI-CNS. The thermodynamic parameters explain that the present adsorption system was measured as feasible and spontaneous [72].

2.6. Ions of various metals.

Given that the experiments were conducted under different conditions, comparing the data produced by different groups of authors is incorrect. The sorption capacity data are comparable when the experiments are conducted under the same conditions. However, taking into account that the studies [60-62, 64, 71] were carried out by the same team of authors and under the same conditions, the maximum heavy metal ions sorption capacity data can be ranked as follows: Zn (25.0mg/g) > Cd(22.1mg/g) > Cu(20.0mg/g) > Ni(18.9mg/g).

Thus, [73] presents a study of the adsorption of Mn(II) and Cr(VI) ions by CNS modified with a 1.0mol/dm ^{3} H_2SO_4 solution at a rate of 1:10(m/v) with constant stirring for 4h at 60°C. It was found that at an initial concentration of Mn(II) and Cr(VI) ions equal to 5mg/dm^3, the ion removal rate under dynamic conditions was 53.1 and 56.4%, respectively, at an initial concentration of 10mg/dm^3 – 10.3 and 10.0%, respectively. The maximum sorption capacities for Mn(II) and Cr(VI) ions were 9.82 and 10.79mg/g, respectively [73].

In work, [74] analyzed the CNS as a natural adsorbent in removing Cd^{2+}, Pb^{2+}, and Cr(III) ions from contaminated water. Further, pHPCZ of CNS lay between 3.69 and 4.01. The best adsorption conditions of the ions Cd^{2+}, Pb^{2+}, and Cr(III) were pH~5.0; adsorbent mass: 12 g/dm^3, equilibrium time 60min. Adsorption isotherms are described identically by the Langmuir, Freundlich, and Dubinin-Radushkevich models. The values of the maximum sorption capacity determined based on the Langmuir equation were 11.23mg/g for Cd^{2+} ions, 8.42mg/g for Cr(III) ions, and 28.65mg/g for Pb^{2+} ions. Pseudo-second order and D–R models suggested the predominance of the chemo-sorption process. Adjustment of Langmuir and Freundlich models suggested adsorption in mono- and multilayers. A thermodynamic study showed that the process was spontaneous for Cd^{2+} ions at 15 and 25°C. CNS had high desorption rates for Cd^{2+} and Pb^{2+} ions but low desorption with Cr(III) ions [74].

CNS after chemical modification with H_2O_2, H_2SO_4, and NaOH to remove Cd^{2+}, Pb^{2+}, and Cr(III) ions in aqueous medium. FTIR analysis confirms the presence of hydroxyl, aliphatic, phenolic, and carboxylic acid groups, as well as favorable adsorption characteristics. The adsorption isotherms for Cd^{2+} and Pb^{2+} ions are most accurately described by the Langmuir model and the Freundlich model for Cr(III) ions. It was found that NaOH solution treatment resulted in a noticeable increase in the maximum sorption capacity for Cd^{2+} and Cr(III) ions. Treatment with H_2SO_4 solution in all cases results in a decrease in the sorption capacity. Modification of CNS with H_2O_2 solution reduces the sorption characteristics of Cd^{2+} and Pb^{2+} ions. The optimum adsorption conditions were as follows: pH~5.0; relation of adsorbent mass/volume of water: 4g/dm^3; 40min of contact time for reaching the equilibration. Results suggest the predominance of chemisorption of Cd^{2+} and Cr(III) ions [75].

Entirely opposite results were obtained in [76]. It is stated that CNS treatment with H_2SO_4 solution contributes to a multiple increase in the sorption capacity of modified materials for Cd^{2+}, Cu^{2+}, Ni^{2+}, and Zn^{2+} ions compared with native CNS samples described in [60-62, 64, 71]. The maximum adsorption capacity values of the modified CNS were 406.6mg/g for Cu^{2+} ions, 436.7mg/g for Cd^{2+} ions, 455.7mg/g for Zn^{2+} ions, and 456.3mg/g for Ni^{2+} ions. It was found that the Langmuir model more accurately describes all isotherms, and the kinetics of the process follow the pseudo-second-order model. The results show that the adsorption of metal ions onto the STCNS was spontaneous and exothermic. The negative value of ΔG° indicates the adsorption process is feasible and spontaneous like adsorption, the negative value

of ΔH° value suggests the exothermic nature of adsorption, and the ΔS° can be used to describe the randomness at the STCNS solution interface during the adsorption [76].

Also, there was a study of the adsorption of metal ions from water by cashew nut testa tannin resin (CATAR), and the effects of temperature, initial pH, initial concentration, and time were investigated. Kinetic studies show that CATAR adsorption is complex, and thermodynamic parameters are, and the calculated thermodynamic parameters reveal spontaneous and endothermic adsorption of studied pollutants onto CATAR. The use of CATAR as an alternative adsorbent is proposed considering that simulated wastewaters gave excellent removal performances of 94.0% (Cd^{2+} ions), 99.4% (Cu^{2+} ions), and 97.1% (Pb^{2+} ions) at pH=6 and 303K [77].

Components of the liquid CNS extraction phase can also remove metal ions. CNSL-based oxime was synthesized to extract Co^{2+}, Ni^{2+}, and Mn(II) from aqueous solutions. The ratio of metal ions in the solution was 1:1:1. All metals were successfully extracted between pH=4-6. The loaded organic phase was subsequently stripped with an acidic solution. The extraction efficiency of the CNSL-based extractant was similar to that of a commercial phenol-oxime extractant. The metals were stripped from the loaded organic phase with a recovery rate of 95% at a pH=6 [78].

It is shown that in addition to metal ions, CNSL can remove halogens from water. A promising case of separation of non-radioactive iodine from an aqueous solution using neem oil phenolic resin treated with lignocellulosic biomass was presented. The resin used to treat lignocellulosic biomass was prepared using CNSL and phenol-formaldehyde. The iodine sorption followed the Langmuir isotherm, indicating a monolayer surface adsorption reaction. The kinetics of the process are most accurately described by the pseudo-second-order model. The maximum iodine removal efficacy of the resin-treated biomass was 3.64mg/g [79].

3. The use of cashew nut shells to remove dyes and phenol from aqueous media

Agricultural raw materials process waste provides good sorption materials to remove organics from aqueous environments, as shown by numerous literature reviews [80-84]. A literature review showed that CNS was also used to remove various phenol dyes from aqueous environments.

Thus, in particular, CNS was studied as an adsorbent for removing Methylene blue (MB) dye from aquatic solutions. The maximum MB adsorption was obtained at pH~10.0; the monolayer adsorption capacity was found to be 5.311mg/g, and the equilibrium was reached for 60min. Freundlich isotherm model gives the best fit to the experimental data. The kinetic data showed that the pseudo-second-order kinetic model better matches the observed adsorption behavior of MB onto CNS. The thermodynamic calculations indicated the exothermic and spontaneous character of the adsorption of MB dye on CNS at 30-60°C. A Boyd kinetic plot confirms that the external mass transfer is the slowest step involved in the adsorption process [85]. CNS sorption characteristics for the above dye can be improved by treating CNS with an H_2SO_4 solution. Modified CNS's maximum sorption capacity for methylene blue dye increased to 71.33mg/g. It was also found that the Freundlich isotherm model best fitted the equilibrium data. Boyd's kinetic model was applied to describe the adsorption mechanism, and the results show that the pseudo-second-order equation fits the kinetic data very well [86].

Also, CNS has been utilized as an adsorbent to remove Congo red (CR) dye from an aqueous solution. It is found that the adsorption isotherm is described identically (R^2=0.999) by the Freundlich, Redlich–Peterson, Koble–Corrigan, Sips, and Toth models. The maximum sorption capacity of CNS by CR was 5.18mg/g [87]. The optimum values of pH, adsorbent dose, initial dye concentration, time, and temperature were found to be 3.2, 24.76g/dm^3, 20mg/dm^3, 67min, and 30°C for complete removal of CR dye, respectively [84]. Thermodynamic parameters such as ΔG°, ΔH°, and ΔS° have also been evaluated, and it has been found that the sorption process was feasible, spontaneous, and exothermic. It was shown that the adsorption of CR could be described by the pseudo-second-order equation, suggesting that the adsorption process is presumably a chemisorption [87,88].

CNS sorption characteristics can be improved by using NZVI-CNS as a sorbent. Response surface central composite design methodology was used to find the interaction among the variables and determine the optimum condition for the adsorption of CR dye from the aqueous solution. The optimum values of pH=6, adsorbent dose 2g/dm, initial dye concentration 40mg/dm^3, time 30min, and temperature 40°C were found to be and for complete removal of CR dye. The experimental values were in good agreement with predicted values, with R^2=0.9948 [89].

Tea waste (TW) and CNS are employed in removing Acid Green 25 dye from aqueous media. It was found that BET surface area was obtained as 25.70 and 68.82m^2/g for CNS and TW, respectively. Maximum adsorption was achieved at a pH=1 using TW and CNS. Adsorbent loading was established at 0.15g of TW and 0.2g of CNS. Maximum uptake capacities were obtained as 123.46 and 76.34mg/g for TW and CNS, respectively. The Langmuir model has well-exemplified equilibrium data, whereas kinetic data is suited well to the pseudo-second-order equation for dye removal using TW and CNS. Evaluation of thermodynamic parameters confirmed the spontaneous and physical nature of the studied adsorption [90].

Adsorption of dyes from water by cashew nut testa tannin resin (CATAR) was studied. Kinetic studies show that CATAR adsorption is complex, and thermodynamic parameters are, and the calculated thermodynamic parameters reveal spontaneous and endothermic adsorption of studied pollutants onto CATAR. Removal performances obtained for simulated dye wastewaters using CATAR at similar conditions for removal give 71.1%, 79.2%, and 86.6%, respectively, for crystal violet, methylene blue, and malachite green dyes with sorbent dosage of 3g/dm^3 [77].

The work describes the robust biosynthesis of AgNPs using aqueous extract of A. occidentale testa. Reductive-degradation of azo dyes such as CR and methyl orange (MO) was manifested using *Anacardium occidentale* testa derived silver nanoparticles (AgNPs) as a catalyst. The AgNPs are mainly in a distorted spherical shape with an average size of 25nm. The CNS-derived AgNPs show excellent catalytic behavior on the reductive degradation of CR and MO with $NaBH_4$ assistance. The calculated rate constants for the degradation of CR and MO are 0.0795 and 0.1178min^{-1} [91].

There are several studies on removing phenol from aqueous media using CNS as a sorbent. Studies [92] showed that the pH of aqueous solutions affected phenol removal due to a decrease in removal efficiency with increasing solution pH. Equilibrium data fitted well with the Langmuir model with a maximum monolayer adsorption capacity of 5.405mg/g. Thermodynamic parameters such as ΔG◦, ΔH◦, and ΔS◦ have also been evaluated, and it has

been found that the sorption process was feasible, spontaneous, and exothermic. It was shown that the adsorption of phenol could be described by the pseudo-second-order equation [92]. CNS sorption capacity for phenol can be improved by modifying the sorbent. Thus, it was found that CNS treatment with a 3M H_2SO_4 solution increases the maximum sorption capacity for phenol to 35.08mg/g [93].

Even greater sorption characteristics were achieved when phenol was extracted from simulated solutions using NZVI-CNS. It was found that with the initial phenol concentration of 60mg/dm^3, contact time 30 minutes, T =50°C, and pH =6, the phenol removal rate is 96.88% [94].

4. Use the use of cashew nut shells for activated carbons and carbonates production and the use of the latter to remove pollutants from aqueous media

Given the high density of CNS and other cashew processing waste, one of the application areas is activated carbons and carbonized production, as well as research and application of the latter to remove various pollutants from aqueous media.

Thus, cashew nut processing waste, including cashew skin, cashew shell, and cashew shell de-oiled cake, was pyrolyzed in an anoxygenic environment at temperatures of 300-500℃ at a heating rate of 10℃/min in a lab scale glass-tubular reactor under an inert atmosphere of nitrogen with a flow rate of 50 sm^3/min. At all the slow pyrolysis temperatures, cashew skin led to more biochar yield (40wt%) as compared to cashew de-oiled cake (26wt%) and cashew shell waste (22wt%) [95].

A study was conducted on the characteristics of microwave-assisted pyrolysis products of CNS. The pyrolysis process of CNS was conducted with microwave heating of 400W for 60 minutes. Pyrolysis products such as bio-gas, bio-oil, and bio-char were identified. Biochar and bio-oil production are about 35% and 45%, while 20% of the by-products are water and bio-gas. There is a significant e in the volatile matter, and fixed carbon of derived biochar, and the porous structure was observed in a range of macropores after pyrolysis. The TGA profile reveals CNS sample lost about 71.25% of mass before reaching 750℃. Bio-oil yield has a density of 1.036gr/ml, and a viscosity of 19.5cst after water removal [96].

CNS was characterized and slow pyrolyzed in a simple batch-type reactor. The experiments were performed using nitrogen or air as carrier gases. CNS showed a high heating value of 20.7 MJ/kg,which is among the highest found for different types of biomass. Pyrolysis under nitrogen flow showed a yield of solid, liquid, and gas products of 30, 40, and 30wt%, respectively. Under air flow, an increase in the gas phase (46wt%) was observed with a decrease in biochar production, mainly, bio-oil. The biochars have high carbon content (70–75wt%) and high heating values in the 25–28MJ/kg range, presenting suitable properties for energy sources. The gas phase revealed the predominance of CO_2 and CO at temperatures lower than 400°C; above this temperature, there was a preferential formation of H_2 [97].

Also, CNS were carbonized at 500°C for 3 hours. Then, the charcoal was activated at 800°C and 1000°C for 60 minutes. The results showed that the frequency of pores in charcoal activated at 1000°C tended to be higher than that of charcoal activated at 800°C. The higher activation temperature increased the pore diameter of the charcoal and decreased the clogging residue. Thus, the pore diameter of the activated carbon (AC) sample produced at 800°C is 3.73-21.44μm, and at 1000°C – 12.76-55.70μm [98].

The total areas of AC made from CNS varied (102-m^2/g) [99-117] and were used to remove heavy metal ions and dyes from aqueous environments. Thus, adsorptive removal of Cd^{2+} ions from aquatic solution using the AC prepared from (1:1) coconut shell and CNS. The quantitative removal of 100sm^3 of 10mg/dm^3 of Cd^{2+} ions occurred when batch studies were carried out at an optimum pH=4.0, AC dose of 0.04g, and equilibration time of 45 minutes with the carbon composite. The Langmuir isotherm was found to be suited. Kinetic studies were fitted best with a pseudo-second-order model. The Cd^{2+} ions adsorbed were quantitatively desorbed with 0.1M HCl [99].

CNS was converted into AC powders using KOH activation plus CO_2 gasification at 1027K. AC derived from KOH/char ratio equal to 1 and CO_2 gasification time from 20 to 150min. were exhibited the BET surface area increasing from 222 to 627m^2/g. and those were derived from KOH/char ratio of 4 with an activation time of 20 to 150 min. exhibited a high BET surface area from 682 to 1026m^2/g. The adsorption of Cd^{2+} and Pb^{2+} ions was investigated. The maximum capacity of Pb^{2+} and Cd^{2+} ions was found to be 28.90mg/g and 14.29mg/g, respectively [100].

Cd^{2+} and Pb^{2+} ions adsorption by AC produced from CNS carbonized at 500°C for 4 h was also studied. The total AC surface area was 512m^2/g. It is found that the Freundlich model more accurately describes Cd^{2+} and Pb^{2+} ions adsorption isotherms. Moreover, Cd^{2+} and Pb^{2+} ion adsorptions followed second-order kinetics. The maximum sorption capacity for Cd^{2+} ions was 2.87mg/g, and for Pb^{2+} ions – 2.61mg/g [101].

AC prepared from CNS using potassium hydroxide activation at 850°C in N_2 and CO_2 atmosphere was used as an adsorbent to remove Cr(III) ions from aqueous solutions. It was determined that the AC had a BET surface area of 1,120m^2/g, pore volume of 0.5789cm^3/g, average pore size of 22.57nm, and bulk density of 0.553g/cm^3. The Freundlich and Langmuir isotherm fitted well to Cr(III) adsorption data. Cr(III) uptake capacity was 13.93mg/g, which was calculated from the Langmuir isotherm [102].

AC from CNS was studied to remove Cu^{2+} and Cr(III) ions from model solutions. The maximum sorption capacity for Cu^{2+} and Cr(III) ions was found to be 49.8mg/g and 41.17mg/g, respectively. The fit of the Langmuir isotherm was better for the experimental data of Cu^{2+} and Cr(III) ions, indicating adsorption in monolayers. Adsorption kinetics were better adjusted to the pseudo-second-order model [103].

AC prepared from CNS and modified by grafting polyethyleneimine onto the surface were tested for removal of Cr(VI) ions. The removal efficiency of AC without and with polyethyleneimine decreased with increased pH, with maximum efficiency found at pH=2. AC's average maximum adsorption capacities were calculated to be 340 ± 20mg/g and 320 ± 20mg/g for unmodified and modified carbons, respectively [104].

In addition, it was shown that AC from CNS can be used to reduce groundwater hardness [105].

AC and carbonizates from CNS were also used to remove dyes from simulated solutions and wastewater. In particular, there are several publications on the removal of MB AS dye from CNS. It is determined that MB pore size and maximum sorption capacity depend on temperature. The maximum values are reached at CNS thermal exposure temperature of 850°C [106].

[107] shows that the maximum sorption capacity determined from the Langmuir equation was 68.72mg/g at pH =10. It was found that the adsorption isotherm is well described

by the Redlich-Peterson model (R^2=0.989), and the process kinetics corresponds to the pseudo-second-order model (R^2=0.999). [108] shows that MB's highest sorption capacity (92.0mg/g) is achieved at pH=10, and the adsorption isotherm is most accurately described by the n-layer BET model [108]. MB adsorption could reach 352mg/g with CNS activated by CO_2 [109] and 226mg/g with CNS activated by steam [110]. MB adsorption capacity by the chemical activation of CNS with $ZnCl_2$ was advanced to 476mg/g [111].

AC produced from CNS by physical or chemical modification was studied to remove MB dyes from simulated solutions. The chemical carbon showed remarkable MB color removal efficiency compared to the physical carbon. In the trials with varying parameters, the physical carbon showed 88.75% (at 40ppm initial concentration) of maximum color recovery, whereas the chemical carbon showed 91% (at 50ppm initial concentration) [112].

In [113] the study presented here AC (Commercial), charcoal (CNS), and charcoal (Wood) were used as an adsorbent to remove MB dye from solutions with a dye content of 2% and 5%. Experimentally, it is observed that the concentration of dye affects the adsorption results. At 5% concentration of MB dye, the rate of adsorption for AC is higher than that of a 2% concentration of dye. Meanwhile, for the other two adsorbents, the percent drop in concentration is almost the same at 2% and 5% in MB dye concentration [113].

CNS AC was prepared by chemical activation with KOH at two different ratios and was studied to remove the Brilliant green (BG) dye. The ratio 1:1 has given a high surface area of 407.80m^2/g and a high pore volume of 0.29cm^3/g. The BG dye adsorption isotherm of CNS AC can be better fitted with the Langmuir model, with a maximum adsorption capacity BG of 243.90mg/g [114].

Synthesis of titanium dioxide (TiO_2) nanoparticles and TiO_2 loaded CNS AC (TiO_2/CNS AC) was undertaken using the sol-gel method, and their application in BG and MB dye removal under sunlight radiation has been investigated. Contact time experiments were run with an optimum dosage of TiO_2 and TiO_2/CNS AC (0.25 and 0.2g/dm^3) in 10mg/dm^3 dye solutions at a constant solution pH of 6.7 for 120 min under sunlight. It is observed that TiO_2/CNS AC is more efficient at all experimental intervals. The removal of BG and MB using naked TiO_2 reached 86.23% and 84.75%, respectively, after 120 min irradiation time. In the case of TiO_2/CNS AC, the removal of BG and MB reached 99.75% and 96.35% after the same irradiation time [115].

Low-cost carbons were prepared from palm nut shells, CNS, and broomsticks using a sulphuric acid process and characterized. The activities of these carbons (PNSC, CNSC, and BSC) were compared with those of high-cost commercial activated carbon. The effect of pH, time, and carbon dose were examined along with isotherm studies. The application of these carbons was examined in the color removal of Dark green PLS from both effluent samples and synthetic samples [116].

Also, AC was prepared from CNS by chemical activation with phosphoric acid as tested for acetaminophen removal. It was found that an increase in carbonization temperature resulted in increased pore volume and decreased amount of surface functional groups. Detailed surface characterization indicated the involvement of surface functional groups in removing acetaminophen either via hydrogen bonding or by acid hydrolysis. The carbon obtained at 600°C, which contains many carboxylic groups and high pore volume, exhibited the highest adsorption capacity [117].

5. Conclusions

The paper summarizes literature data on the use of Cashew nut shells as sorption materials to remove ions of various metals and metalloids (Cd^{2+}, Co^{2+}, Cr(III), Cr(VI), Cu^{2+}, Mn(II), Ni^{2+}, Pb^{2+}, Zn^{2+}), dyes and phenol from aqueous environments. Brief information is provided on the amount of cashew nut shells generated, their chemical composition, and their recycling applications in various industries. The paper also provides Cashew nut shell adsorption process parameters for the pollutants in question. It is shown that Cashew nut shell treatment with various chemicals improves sorption characteristics for various pollutants. It was found that adsorption isotherms are described by various models, most often by those of Langmuir and Freundlich. In most cases, the process kinetics follows the pseudo-second-order model. It is also shown that a Cashew nutshell is a good precursor for activated carbons and carbonizates production, which can also be used to remove various organic and inorganic pollutants from aquatic environments.

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Conflicts of Interest

The authors declare no conflict of interest.

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