

Using Quercus Waste and Biomass Components to Remove Pollutants from Aquatic Environments (a Literature Review)

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Abstract: The paper summarizes literature data on the use of waste (sawdust, shavings) and biomass components (leaves, bark, acorns) of *Quercus* trees and the extracts from the above components to remove metal ions (Cd^{2+} , Cr(III), Cr(VI), Cs^+ , Cu^{2+} , Fe^{2+} , Hg^{2+} , Ni^{2+} , Pb^{2+} , and Zn^{2+}) and various dyes from aqueous media. It provides brief information about the composition of *Quercus* trees components. It gives the adsorption process parameters and the values of sorption parameters for the studied pollutants. It was shown that chemical modification with various chemical reagents could increase oaks waste and biomass components' sorption characteristics for various pollutants. It was found that most adsorption isotherms are most accurately described by the Langmuir model and less often by the Freundlich model. The process kinetics mainly follows the pseudo-second-order model.

Keywords: waste and biomass components; extracts; *Quercus* trees; metal ions; dyes; removal.

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1. Introduction

Currently, the world community is rapidly developing a new promising environmental protection area – the use of agricultural waste (straw, grain husks, cakes, leaves, etc.) [1-5] and wood biomass (sawdust, shavings, wood chips, etc.) [6-10] and tree components (bark, leaves, needles, fruit shells, etc.) [11-15] as reagents to remove various pollutants from water environments.

Of particular interest are wood biomass components due to the high tonnage of annual formation, high adsorption characteristics for various pollutants, ease of collection and modification, etc. There are many international reports about the use of biomass from various trees as sorption materials, in particular, *Azadirachta indica*, mango (*Mangifera indica*), and others.

This review summarizes information on the use of oak trees' biomass components and sawdust as sorption materials. Oak (*Quercus*) is a genus in the Beech (*Fagaceae*) trees and shrubs family. The genus includes about 600 species. The natural habitat of the oak includes the temperate regions of the Northern Hemisphere. The southern boundary of the habitat is the tropical highlands; several species are also found south of the equator. Oak wood is strong, <https://biointerfaceresearch.com/>

solid, dense, hard, and heavy. Wood properties depend on the growing conditions of the tree. Oak wood is an excellent building and craft material: it is used for underwater and land structures, underwater and main parts of wooden ships (mainly summer oak), and as a barrel, cart, machine, furniture, parquet, and carpentry wood (preferably winter oak); for the latter, stained oak is particularly valued, water-seasoned for a long time (up to hundred years), with its dark, almost black wood [16].

The chemical composition of oak wood trees varies significantly depending on many factors, including the wood species [17]. The *wood composition of the Quercus (Q. robur, Q. alba, Q. prinus, Q. stellate, Q. rubra, Q. lyrata)* depends on the species. The content of cellulose was found to be 38.0-45.7%, hemicellulose 22.2-30.0%, lignin 22.0-29.6%, extractable substances 3.8-6.6%, and ash content 0.3-0.5% [18].

The representatives of the first group, after hydrolysis by acids or enzymes, form gallic and ellagic acids. From the chemical point of view, they are esters of benzoic and p-hydroxy-cinnamic (coumaric) acids of the general formulas given in Figure 1.

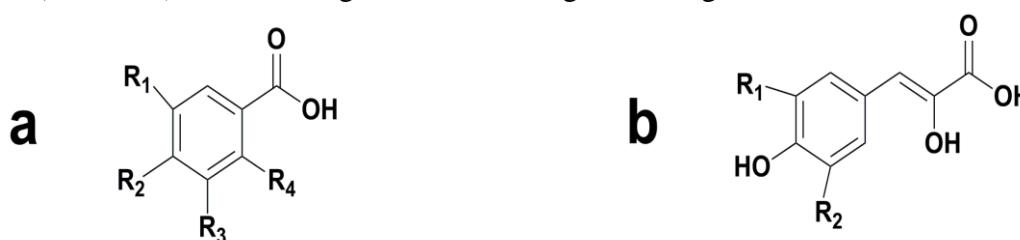


Figure 1. General formulas of tannins in oak wood: (a) benzoic acid, (b) coumaric (hydroxy-cinnamic) acid.

Multiple researchers [19-27] have found the following chemical acids listed in Table 2 and corresponding aldehydes in extracts from wood and other components (bark, leaves, acorns, rhizome) of oak trees.

Table 2. Chemical compounds in oak wood.

Chemical name	Formula
Gallic acid (Figure 2a)	R1 = R2 = R3 = OH, R4 = H
Gentisic acid (Figure 2a)	R1 = R4 = OH, R2 = R3 = H
p-hydroxybenzoic acid (Figure 2a)	R2 = OH, R1 = R3 = R4 = H
Protocatechic acid (Figure 2a)	R1 = R4 = H, R2 = R3 = OH
Syringic acid (Figure 2a)	R1 = R3 = OCH ₃ , R2 = OH, R4 = H
Salicylic acid (Figure 2a)	R1 = R2 = R3 = H, R4 = OH
Vanillic acid (Figure 2a)	R1 = R4 = H, R2 = OH, R3 = OCH ₃
Coumaric acid (Figure 2b)	R1 = R2 = H
Caffeic acid (Figure 2b)	R1 = H, R2 = OH
Ferulic acid (Figure 2b)	R1 = H, R2 = OCH ₃
Sinapic acid (Figure 2b)	R1 = R2 = OCH ₃

The presence of a large number of OH groups in the tannins, which are part of oak wood chemical compounds, helps remove heavy metal ions from aqueous solutions.

2. Use of Oak Sawdust to Remove Various Pollutants from Aquatic Environments

English oak (*Quercus robur*) sawdust was studied to remove Cu²⁺ ions from aqueous solutions [28-32]. It is found that the highest sorption rates were achieved when treating sawdust with 3 N aqueous NaOH solution at 22°C [29]. At the initial 0.01 M Cu²⁺ ions concentration in the solution, the removal rate of the latter was 89% during 60 minutes of contact at pH = 3 and the dosage of the sorption material of 12g/dm³ [30]. It is shown that an increase in the copper ions concentration in the solution from 0.001 to 0.01 mol/dm³ resulted in a decrease in the removal efficiency from 99.5 to 80%. A slight increase in the removal

efficiency is observed when using a combination of oak sawdust with activated carbon in various ratios [31].

The utilization of H₂SO₄-modified oak sawdust (*Quercus* L.) (HMOS) as a new and promising sorbent for the uptake of an extremely toxic inorganic pollutant, Cr(VI) ions, from aqueous media by batch adsorption method has been investigated. The maximum Cr(VI) ions uptake was achieved at initial solution pH = 2.5 and at an equilibrium time of 240 min. The adsorption behaviors of Cr(VI) ions onto both natural oak sawdust (NOS) and HMOS were analyzed in terms of Langmuir and Freundlich isotherm models, and the Cr(VI) ions adsorption was obtained to be compatible with both isotherm models. The Cr(VI) ions adsorption capacities of NOS and HMOS were calculated as 48.07 and 100.00 mg/g, respectively, by utilizing the Langmuir model [32].

The sorption of Cs⁺ ions by various wood species, including English oak (*Quercus robur*) was studied using ¹³⁴CsCl as a tracer [33]. It was shown that the sorption capacity of oak wood reached 8mg/g for these ions and increased in the case of using rotten wood.

A new wood chips-ZrO₂ biosorbent (W-ZrO₂) was synthesized using wood residue material generated from the *Quercus robur* tree during furniture manufacturing. Biosorbent was tested for the simultaneous removal of both chromium (Cr) ions: Cr(III) and Cr(VI), in the binary component solution. The optimal pH for simultaneous removal of both Cr(III) and Cr(VI) chrome ions is pH = 4.0, with removal efficiency over 99.5 % in both cases. Equilibrium experimental results are best fitted by the Langmuir sorption isotherm model. The maximal sorption capacities of the biosorbent for simultaneous removal of Cr(III) and Cr(VI) ions in the binary-component system are 16.18 and 83.52 mg/g, respectively [34].

The sorption of Si²⁺, Fe²⁺, and Zn²⁺ ions by the sawdust of various tree species, including oak, was studied. It was established that at the initial 10mg/dm³ concentration of these ions and the 10g/dm³sawdust concentration in simulated solutions, the removal rate of Cu²⁺ ions was 51%, Zn²⁺ ions - 50%, Fe²⁺ ions - 44%. At the initial metal ions concentration of 50mg/dm³, the removal efficiency was 28, 29, and 36%, respectively [35].

The sorption characteristics of oak sawdust can be improved by chemical modification of the latter. It is reported that the study of sorption purification from Cu²⁺, Ni²⁺, and Cr(VI) ions by sawdust of kermes oak (*Quercus coccifera*) treated with HCl solutions at 20 =⁰C. The experiments have shown that the greatest Si²⁺, Ni²⁺, and Cr⁶⁺ ions removal rates were provided by an increase in the dosage and time of contact of sawdust with sorbate. It was noted that the pH value significantly affects the sorption efficiency. It was determined that the greatest C²⁺ ions removal rate (94%) is achieved at pH = 4 and sawdust dosage of 40g/dm³, Ni²⁺ ions (82%) – at pH = 8 and_{sawdust} = 30 g/dm³, Cr(VI) ions (84%) – at pH = 3 and_{sawdust} = 60 g/dm³[36]. Sorption isotherms for these metal ions at the initial concentration of the latter from 0.01 to 100 mg/dm³ are plotted and calculated using the Langmuir and Dubinin-Radushkevich equations. It is shown that the isotherms were more adequately described by the Langmuir model (R² = 0.92-0.99), and the sorption kinetics follow the pseudo-second-order model. The thermodynamic process parameters at T = 293-313 K were determined.

It was determined that the ΔG value during adsorption of Cu²⁺ ions is -2.840- -3.330 kJ/mol, Ni²⁺ – ions -2.898- -3.156 kJ/mol, Cr (VI) ions – -1.295- -1.446 kJ/mol. The ΔN values for these ions were 4.331 kJ/mol, 0.876 kJ/mol, and 0.908 kJ/mol, ΔS values were 0.024 kJ/mol • K, 0.013 kJ/mol • K and 0.008 kJ/mol • K, respectively [36].

Along with heavy metal ions, oak sawdust was studied for the sorption of various dyes from simulated solutions. The Methylene blue dye is most often used as a reference for studying

the sorption characteristics of various sorbents [37]. Oak sawdust was also used to study the sorption of the said dye from aqueous solutions [38-41]. In particular, the sorption of the Methylene blue dye from aqueous solutions with an initial concentration of 1000mg/dm³ by native oak sawdust was studied [38]. The maximum sorption capacity was found to be 29.94mg/g. It was determined that the adsorption isotherm was more adequately described by the Langmuir equation, and the adsorption kinetics follows the second-order model. At the same time, it was determined in [39] that sorption is most fully described by the Freundlich equation, and sorption kinetics is more clearly described by the pseudo-second-order model.

The sorption process parameters were determined for Methylene blue dye removal at an initial concentration of 200mg/dm³ at 22°C: pH = 12, t = 120 min, C_{sorp} = 5g/dm³. It was determined that the sorption isotherms were more fully described by the Freundlich equation (R² = 0.9888), and the sorption kinetics followed the pseudo-second-order model with intraparticle diffusion. The thermodynamic parameters of the sorption process were determined.

The thermodynamic parameters of the process were determined, which were in the temperature range 295-333 ° C: ΔG = -2.43 - -9.12 kJ/mol, E_a = 52.2-52.5 kJ/mol, ΔN = 49.75 kJ/mol, ΔS = 177.67 J/mol • K. The thermodynamic parameters indicate that adsorption is a spontaneous and endothermic process. The activation energy is higher than 42kJ/mol, which indicates a controlled chemical process [40].

In the case when sawdust is treated with 0.1 N sulfuric acid solution, the authors of [41] arranged the adequacy of the models for describing the sorption isotherm in a row according to R² value: Langmuir > Tyomkin >> Freundlich, which contradicts the above information.

Sawdust of 10 tree species, including those of English oak (*Quercus robur*) and sessile oak (*Quercus petraea*) was used to remove methylene blue from simulated solutions. It was revealed that under the following experiment conditions (C_{dye} = 50mg/dm³, t = 120min, T = 298.15K, Sorbent = 10 g/dm³, 150 rpm), the extraction efficiency of the said dye exceeded 95% [42].

Has been made to use oak (*Quercus coccifera*) sawdust as a potential adsorbent for basic dye (Astrozone Blue FGRL) removal from an aqueous solution. The experimental data at four initial dye concentrations (25, 50, 100, and 200 mg/dm³) were analyzed by the pseudo-first-order, pseudo-second-order, Elovich, and intra-particle diffusion kinetic models. Thermodynamic parameters, enthalpy change (ΔH = 19.44 kJ/mol), entropy change (ΔS = 81.77 J/mol•K), and Gibbs free energy change (ΔG = -4.519, -5.336 and -6.154 kJ/mol at 293, 303 and 313 K) were calculated for the uptake of the dye and indicated that the adsorption was a spontaneous and endothermic process. Kinetic studies of the data showed that the adsorption follows the pseudo-second-order kinetic model [43].

Kinetic and thermodynamic characteristics of Methyl orange dye sorption by hardwood sawdust, including oak (*Quercus robur*), were studied. The initial dye concentration was 0.005-0.12 mg/dm³, and the maximum sorption capacity calculated from the Langmuir equation was 0.013 mg/g. It is found that the isotherm of sorption by oak sawdust was most clearly described by the Freundlich equation (R² = 0.981), and the kinetics of the sorption process corresponded to the pseudo-second-order model (R² = 0.9957) [45].

The aim of the study was to screen the waste wood biomass of 10 wood species, including sawdust of *Quercus robur* and *Quercus petraea*, as biosorbents for the elimination of the artificial dye Congo Red (CR) from water. According to the findings, the efficiency of CR removal increased as biosorbent concentration and contact duration increased. Sorting

waste biomass from various wood types to use as biosorbents to remove CR from aqueous solutions ($With_{CR} = 50 \text{ mg/dm}^3$, $With_{\text{sorbent}} = 10 \text{ g/dm}^3$, $t = 360 \text{ min}$, $T = 298.15 \text{ K}$, $v = 150 \text{ rpm}$) showed that the efficiency of the dye removal by sawdust of *Quercus robur* and *petraea Quercus* amounted to 32.1 and 29.0 %, respectively [46].

Oak sawdust was also used for adsorbing 10 dyes, of which 3 dyes, viz. Direct Orange 8, Direct Brown 2, and Basic Blue 86, showed the highest values of the maximum sorption capacity, which amounted to 6.36, 9.3, and 33.47mg/g, respectively [47].

Oak sawdust pretreated with cetyltrimethylammonium bromide was studied to extract the Food Green 3 dye from simulated solutions. The maximum sorption capacity was found to be 36.6mg/g. It is found that the sorption isotherm was more adequately described by the Freinlich equation, and the adsorption kinetics was described by the Elovich model. Calculated values of the free energy of biosorption, based on the Dubinin-Radushkevich equation ($E < 8 \text{ kJ/mol}$) and thermodynamic studies ($0 < \Delta G^\circ < -20 \text{ kJ/mol}$), indicate a spontaneous physisorption [48].

In addition to sawdust, oak wood processing gives chips and shavings. The latter has also been studied as sorption materials for removing pollutants from aqueous media.

Thus, it is reported that oak petiolate (*Quercus robur*) shavings were studied to remove Cu^{2+} and Cr(III) ions from simulated aqueous solutions. It was reported that the lignin content in the wood under study was 24.9%, and the chip surface area was $317 \text{ m}^2/\text{g}$. At an initial concentration of Cu^{2+} ions in a 0.01 mmol/dm^3 solution and Cr 3^+ ions - 0.0067 mmol/dm^3 , the sorption capacity for these ions was 2.68 mg/g and 1.72 mg/g, respectively [49].

Also, a new lignocellulosic- Al_2O_3 hybrid biosorbent (LC- Al_2O_3) was synthesized using wood residue material from the oak tree (*Quercus robur*). Biosorbent was tested for the simultaneous removal of three different types of pollutants: Cu^{2+} ions, textile dye Reactive Blue 19, and fungicide cyprodinil in the multi-component model solution and natural water. In order to define optimal process parameters for the simultaneous removal of all three pollutants, the effects of pH, temperature, sorbent dose, pollutants concentration, and hydrodynamic conditions on the sorption process were investigated. Sorption of pollutants onto LC- Al_2O_3 was highly pH-dependent, and the optimal pH = 5, with removal efficiency near 98% for all three pollutants. Sorption kinetics followed pseudo-second-order, intraparticle diffusion, and Chrastil's models, which suggest that both surface reaction and diffusion were rate-limiting steps. Equilibrium experimental results are best fitted by the Langmuir sorption isotherm model. The maximal sorption capacities of the biosorbent for simultaneous removal of pollutants in a multi-component system are 15.69 mg/g for Cu^{2+} ions, 29.99 mg/g for Reactive Blue 19, and 20.97 mg/g for cyprodinil [50].

3. Use of Oak Bark to Remove Various Pollutants from Aquatic Environments

As previously mentioned [16], the bark of oak trees contains most of the tannins, which is determinative for using the latter to remove heavy metal ions from aqueous solutions. In this regard, the bark of oak trees has been widely studied as a sorption material to remove various pollutants from aqueous solutions [51, 52].

In particular, the composition of the Austrian oak (*Quercus cerris*) bark was determined in [53]. It was determined that *Quercus cerris* bark consists of 28.5% suberin, 28.1% lignin, and 16.7% extractable substances, and the ash content is 2.6%. Of the non-cellulose monosaccharides, xyloses predominate (27.8% of the total neutral sugars), with arabinose and galactose (11.5% and 7.9%, respectively). Suberin consists mainly of long-chain ω -hydroxy

acids accounting for 90% of all long-chain monomers and including α , ω -diacids (less than 8%) and a small amount of alkane acids C₁₆ and C₁₈, and alkanols C₂₀, C₂₂ and C₂₄. Of particular interest is the use of cork oak (*Quercus suber*) bark as a sorption material, which is widely used for the manufacture of corks for capping wine bottles. The structure, composition, and mechanical properties of *Quercus suber* bark are given in the review [54]. The honeycomb structure of the cork oak bark is interesting. Such structure provides chemisorption and physical sorption on the surface and inside the cells of the sorption material.

The bark of *Quercus cerris* [55] and *Quercus suber* [56] was studied as a sorption material to remove Cr(VI) ions. It was found that using native Austrian oak bark at 25mg/dm³ initial chromium ion concentration resulted in the maximum sorption capacity of 21.69 mg/g at pH = 3 and 48 hours of contact [55]. In the case of native *Quercus suber* bark, the maximum sorption capacity (17.0mg/g) is achieved at pH = 2, other things being equal [56].

Studies have been made on the removal of Cu²⁺ and Ni²⁺ ions by cork oak (*Quercus suber*) bark. It was determined that the greatest removal degree of these ions occurs at pH = 6-7 [57]. The presence of NaCl in simulated solutions contributes to a decrease in sorption efficiency. The maximum sorption capacity for these ions was established at their initial concentration in solution equal to 100 mg/dm³: for Cu²⁺ ions – 2.64mg/g, for Ni²⁺ ions – 4.09mg/g. It is determined that the adsorption isotherms are more accurately described by the Langmuir equation [57].

Cork oak (*Quercus suber*) bark has also been studied as a biosorbent for Cu²⁺, Zn²⁺, and Ni²⁺ ions [58]. The maximum sorption capacity for these ions was 0.63, 0.76, and 0.34meq/g, respectively. It is shown that ion exchange plays a more important role in the adsorption of Cu²⁺ and Ni²⁺ ions than in the adsorption of Zn²⁺ ions. An important role in the chemisorption of these ions is played by carboxyl groups in bark, produced through the Fischer esterification reaction. Cork oak *Quercus suber* bark pretreatment with various chemical reagents was studied to improve sorption characteristics. The studies conducted have revealed that treatment with 0.5M NaCl solution contributes to a 30% increase in the sorption capacity for Cu²⁺ ions. Also, preheating or boiling the bark in alkaline solutions, as well as treatment in NaClO and NaIO₃ solutions, contribute to an increase in sorption capacity by 70-80% [59].

Korean researchers studied the effect of phosphorylation of sawdust and bark of sawtooth oak (*Quercus acutissima*) on the efficiency of Cu²⁺, Zn²⁺, Cd²⁺, and Pb²⁺ ions removal from simulated solutions with an initial ion concentration of 25 or 50 ppm. [60]. The phosphorylated sawdust and bark contained phosphorous of 1.2~1.3% in the treatment for 1 hr and 1.4~1.7% for 2 hrs, regardless of species and tree segments. The sawdust indicated a considerable increase in the adsorption ratio of Cu²⁺, Zn²⁺, and Cd²⁺. However, the adsorption of Pb²⁺ was a little increased. It is shown that phosphorylation of oak wood sawdust increases the degree of removal of these ions compared to bark.

Cr(III), Cu²⁺, Ni²⁺, Pb²⁺, and Zn²⁺ ions sorption by the bark of several tree species, including English oak (*Quercus robur*), was studied. It was found that the maximum sorption capacity for these ions was (mol/g): 0.05, 0.09, 0.06, 0.08, and 0.06, respectively [61].

Hg²⁺ ions adsorption by various sorption materials, including the bark of eastern black oak (*Quercus velutina*), showed that the maximum sorption capacity for these ions was 2mmol/g [62].

4. Use of Oak Leaves to Remove Various Pollutants from Aquatic Environments

The leaves of various tree species have been extensively studied as sorption materials to remove various pollutants from aqueous media [63-66]. Renewable biomass, ease of collection, large sorption surface, and good adsorption characteristics are among the reasons for the effective use of foliage as adsorbents.

Removal of Pb^{2+} , Cd^{2+} , and Cr(VI) ions by using chemically modified *Quercus dilatata* leaves (CMQDL) treated with HNO_3 and $CaCl_2$ solutions. The maximum biosorption capacities for remediation of Pb^{2+} , Cd^{2+} , and Cr(VI) ions via CMQDL were 17.54, 20.408, and 20.83 mg/g, respectively, at the optimal conditions. Freundlich isotherm model best evaluates the equilibrium data with high regression correlation coefficient $R^2 = 0.985, 0.826, \text{ and } 0.919$ for eliminating Pb^{2+} , Cd^{2+} , and Cr(VI) ions, respectively. The kinetic study proposed that the remediation operation best obeyed the kinetic pseudo-second-order model. The calculated thermodynamics functions like change in entropy (ΔS°), change in enthalpy (ΔH°), and Gibbs free energy (ΔG°) revealed that the removal of Pb^{2+} ions via the CMQDL was viable, exothermic, and spontaneous, Cd^{2+} ions were endothermic and spontaneous and Cr(VI) ions was endothermic and non-spontaneous [67].

Oak tree leaves have also been studied as sorption materials to remove heavy metal ions from simulated solutions. Thus, in particular, holm oak (*Quercus ilex*) foliage was studied for the adsorption of Cd^{2+} , Cr(VI), Cu^{2+} , Ni^{2+} , and Pb^{2+} ions [68]. At $10\text{mg}/\text{dm}^3$ initial concentration of these ions in simulated solutions, the authors arranged metal ions in a row according to the removal efficiency: $Ni (62\%) > Cd (53.2\%) > Pb (39.5\%) > Cu (20.0\%) > Cr (8.2\%)$. The possibility of partial regeneration of the sorption material using EDTA sodium salt is shown.

5. Use of Oak Fruits to Remove Various Pollutants from Aquatic Environments

There are a number of publications on the use of oak acorn components as sorption materials, which are a dry single-seeded syncarp lower fruit with a hard leathery pericarp, partially or completely enclosed in a cup. It is assumed that the cup is formed from connate axes and bracts of the reduced inflorescence. Oaks have only one acorn in the cup.

The composition of oak acorns includes a huge amount of organic compounds. [69] provides a review of information on the content of chemical compounds in acorns of oak trees of various species. It is shown that the latter includes both pyrogallol with a mass of 126, particularly trigalloyl hexahydrodiphenoyl glucoside ($m/z = 938$) and pentagalloyl glucoside ($m/z = 940$), as well as many other chemical compounds. The presence of a large number of OH groups in the structure of chemical compounds in oak acorns, as can be expected, will contribute to high sorption characteristics with respect to heavy metal ions.

In light of the above, the adsorption of Cr(VI) ions by Mount Tabor oak (*Quercus ithaburensis*) acorn waste under static conditions was studied [70]. It was determined that the maximum adsorption occurred at $pH = 2.0$. It was found that the maximum sorption capacity was $31.48 \text{ mg}/\text{g}$ with an initial Cr(VI) ions content in the solution of $400\text{mg}/\text{dm}^3$ at 25°C . It was determined that the adsorption isotherms at different temperatures were most adequately described by the Freinlich and Langmuir models, and the kinetics of the process was described by a pseudo-second-order model. The thermodynamic sorption parameters were determined at $pH = 2$ and the initial concentration of Cr(VI) ions of $200\text{mg}/\text{dm}^3$: $\Delta G^\circ = -1.16, -2.80, \text{ and } -$

4.71kJ/mol at temperatures of 298, 318, and 333 K, respectively; $\Delta H = 28.75$ kJ/mol, $\Delta S = 100.43$ J/mol \cdot K [70].

The adsorption of Cr(VI) ions by the shells of English oak (*Quercus robur*) acorns was studied. In an equilibrium time of 420 min, the maximum Cr(VI) ions removal at pH = 2 and pH = 10 was 100 and 97 %, respectively. The sorption data fitted well with the Model for Langmuir binding. Langmuir expression analysis revealed a monolayer sorption capacity of 47.39 mg/ml. g with an equilibrium sorbent dose of 5 g/dm³ and pH = 7. The uptake of Cr(VI) by oak acorns was described by a pseudo-second-order chemisorption model [71].

The ability of *Quercus crassipes* acorn shells (QCS) to remove Cr(VI) ions from aqueous solutions was investigated as a function of the solution pH, ionic strength, and background electrolytes. Cr(VI) ions removal rate increased as the solution pH decreased. NaCl ionic strengths lower than 200 mM did not affect chromium removal. The presence of 20 mM monovalent cations and anions, and divalent cations, slightly decreased the removal of Cr(VI) and total chromium by QCS; in contrast, divalent anions (SO₄²⁻, PO₄²⁻, CO₃²⁻) significantly affected the removal of Cr(VI) and total chromium. The biosorption kinetics of chromium ions followed the pseudo-second-order model at all solution pH levels, NaCl ionic strengths, and background electrolytes tested [72].

Continuous fixed-bed column studies were carried out, utilizing acorn shells from *Quercus crassipes* Humb. & Bonpl. (QCS), in order to remove total chromium and Cr(VI) ions from the aqueous solution. Results from the fixed-bed column experiments demonstrate that total chromium biosorption and Cr(VI) ions removal by QCS depends strongly on the pH of the influent solution. The highest capacities for Cr(VI) ions removal and total chromium biosorption are about 181.56 and 110.35 mg/g and are achieved at influent solution pH = 1.0 and 2.0, respectively. Besides this, total chromium biosorption capacities increased from 104.25 to 116.14 mg/g, 109.07 to 117.44 mg/g, and 85.02 to 129.87 mg/g as bed height, inlet flow rate, and influent Cr(VI) ions concentration increased from 1.7 to 6.5 cm, 0.25 to 1 sm³/min, and 50 to 400 mg/dm³, respectively. X-ray photoelectron spectroscopy and biosorption kinetic studies revealed that QCS is able to remove Cr(VI) ions from acidic liquid solution by means of a complex mechanism that involves the binding of Cr(VI) ions oxyanions to positively charged groups present at the QCS surface, after which the Cr(VI) species are reduced to Cr(III) by adjacent electron donor groups, and the generated Cr(III) ions then become partially bound to the QCS biomass and partially released into the liquid phase [73].

Also, the sorption of Cr(VI) ions at a concentration of 50-200mg/dm³ by Mount Tabor oak (*Quercus ithaburensis*) acorn shells was studied under dynamic conditions [74, 75]. It was determined that at an initial concentration of Cr(VI) ions of 100mg/dm³, the height of the sorption material layer with dimensions of 1-3mm 10cm (10g) and a rate of 10cm³/min, the highest absorption degree for these ions occurred at pH = 2. An increase in the pH of the aqueous medium contributes to a decrease in efficiency.

Pericarps of Algerian *Quercus ilex* and *Quercus suber* were used as Cu²⁺ ions adsorbents in artificially contaminated solutions. The lignocellulosic fractions of *Quercus suber* and *Quercus. ilex* (36.47 \pm 9.1 and 47.66 \pm 9.3, respectively) were characterized by FTIR before and after adsorption. Cu²⁺ ions adsorption range was 23.59-48.06 mg/g for *Quercus suber* and 22.56-38.19 mg/g for *Quercus ilex* when Cu²⁺ ions concentration was 100-500 mg/dm³. Adsorption isotherms and Langmuir and Freundlich models of the *Quercus suber* and *Quercus ilex* lignocellulosic fractions indicated natural Cu²⁺ ions adsorption capacities (Qmax) of 53.76 mg/g and 36.06 mg/g [76].

Dry acorn caps of *Quercus robur* were used as a non-modify natural adsorbent. The batch experiments were carried out to remove copper ions in water that has an initial low concentration (1-2.5 mg/dm³) by the prepared natural adsorbent. It was found that the maximum degree of Cu²⁺ ion removal occurred at pH = 7, E = 45° C, contact time 60 minutes, and adsorbent dosage of 10g/dm³. It was found the removal efficiency was 84%, and the adsorption capacity was 0.336 mg/g [77]. It was found that the adsorption isotherm is more accurately described by the Freundlich model, and the process kinetics follows the pseudo-second-order model [78].

Two biomasses derived from fruit shells of oak (*Quercus ilex*) and casuarina were used for the first time as adsorbents for the retention of copper ions Cu²⁺ and methylene blue by adsorption. The highest capacity of adsorption of methylene blue was founded for activated casuarina, 667 mg/g after 2 h of contact, and 83 mg/g for copper ions by activated oak after 3 h [79].

Investigated the effect of ionic strength and background electrolytes on the biosorption of Ni²⁺ ions from aqueous solutions by the acorn shell of *Quercus crassipes* Humb. & Bonpl. A NaCl ionic strength of 0.2 mM was established to have no effect on the Ni²⁺ ions biosorption, and the biosorption capacity of the heavy metal decreased as the ionic strength increased from 2 to 2000 mM. The background electrolytes (KCl, NaNO₃, Na₂SO₄, CaCl₂, MgSO₄, and MgCl₂) had no adverse effects on the biosorption of Ni²⁺ ions at a concentration of 0.2 mM. However, at background electrolyte concentrations of 2 and 20 mM, divalent cations (Ca²⁺ and Mg²⁺) had greater negative effects on the biosorption of Ni²⁺ ions compared to the monovalent cations (Na⁺ and K⁺).

Additionally, the SO₄²⁻ and Cl⁻ anions affected the biosorption of Ni²⁺ ions. The fractional power, Elovich, and pseudo-second-order models represented the kinetic processes of the biosorption of Ni²⁺ ions adequately [80]. Modeling of the Ni²⁺ ions biosorption kinetic and equilibrium data showed that the best agreement of experimental data was achieved with the pseudo-second-order kinetics model and the Freundlich isotherm model, respectively. The calculated thermodynamic parameters indicated that the Ni²⁺ ions biosorption process was endothermic, non-spontaneous, and chemical [81].

Also, it was to investigate the applicability of removing Pb²⁺ ions from aqueous solutions using an acorn (*Quercus ithaburensis*) shell using a batch adsorption process. Various experimental parameters such as adsorbent dose, pH, and contact time were studied to observe their effects on the Pb²⁺ ions adsorption process. At optimum values of the above-mentioned parameters, more than 90 % removal efficiency was obtained within 2 minutes at acorn shell amount of 1 g/100 sm³, pH range of 2-6 for Pb²⁺ ions with an initial concentration of 100 mg/dm³ [82].

The crushed biomass of acorn cups was used as a sorption material to remove Cr(VI) ions and Basic Red 18 and Acid Red 111 dyes [83]. The sorption material under study was pretreated with a 1 M solution of HNO₃ for 24 hours. It was noted that the adsorption isotherms were adequately described by the Langmuir equation at different pH values of the medium. The values of the maximum sorption capacity calculated from the Langmuir equations were 156.2, 7.99, and 6.54 mg/g for Basic Red 18, Acid Red 111, and Cr(VI) ions, respectively.

6. Use of Oak Tree Component Extracts to Remove Various Pollutants from Aquatic Environments

It should be noted that it is not always possible to achieve high sorption characteristics for various pollutants due to the fact that the adsorption process occurs on the surface of sorption materials only. Recently, a new area in water purification and treatment has been developing, i.e., the use of extracts, particularly those produced from tannin-containing raw materials, such as coagulants, flocculants, and complexing agents [84-88].

In particular, due to their high antioxidant capacity and advantageous reducing qualities for the environment, greenleaf extracts have been utilized as reducing agents in synthesizing numerous nanoparticles. For this comparative analysis of the synthesis of iron oxide nanoparticles for arsenic adsorption, five distinct plant species were used. Black tea leaves (*Camellia sinensis*), oak tree leaves (*Quercus virginiana*), green tea leaves (*C. sinensis*), pomegranate leaves (*Punica granatum*), and eucalyptus leaves were the plants whose leaves were chosen (*Eucalyptus globulus*). Using the leaves mentioned above, iron nanoparticles were created using the green synthesis technique. Kinetic and adsorption isotherm studies were used to evaluate the nanoparticles' capacity for adsorption. Eucalyptus leaf nanoparticles were defined to have the highest arsenic adsorption capacity of 39.84 mg/g, followed by oak leaf nanoparticles with an adsorption capacity of 32.05 mg/g. The experiments showed that the adsorption kinetics obeyed the quadratic pseudo-rate equation and that the Langmuir equation could best describe the adsorption isotherm data. [89].

It also investigates the performance of oak (OL), and mulberry (ML) leaves for synthesized nanoscale zero-valent iron (nZVI) in immobilizing Cu^{2+} and Ni^{2+} ions in contaminated sediment. The leaves were ground with a kitchen chopper, then sieved with a 2 mm sieve and pre-dried at 50°C in an oven for 48 h. The amount of 3.7 g oak leaves was measured and put into a 300 ml conical flask, 100 ml of water was added. The flask was then placed in a stirring bath at 80°C for 20 min [90]. Characterization of synthesized Fe nanoparticles from oak and mulberry leaf extracts demonstrated that they are non-toxic and stable nanomaterials for application in sediment remediation. The effectiveness of the stabilization process was performed by microwave-assisted sequential extraction procedure and single-step leaching tests which were applied to evaluate the metal extraction potential. This research showed that OL-nZVI and ML-nZVI were effective in transforming available Cu^{2+} and Ni^{2+} ions into a stable fraction. The maximum residual percentage of Cu^{2+} ions increased by 76% and 73% and for Ni^{2+} ions by 81% and 80%, respectively, with the addition of 5% OL-nZVI and 5% ML-nZVI [91]. Batch experiments revealed that the adsorption kinetics followed a pseudo-second-order rate equation. The Freundlich model could well describe the obtained adsorption isotherm data, and OL-nZVI showed higher adsorption capacity for Ni^{2+} ions removal than ML-nZVI, while ML-nZVI adsorption capacity was higher for Cu^{2+} [92].

The potential use of nZVI particles as a cheap, natural, and effective catalyst in a phenton system to remove an aqueous Magenta flexographic dye from an aqueous solution is being investigated. The influence of four quantitative parameters on decolorization efficiency was investigated: initial dye concentration (20-180 mg/dm³), OAKnZVI dosage (0.75-60 mg/dm³), H₂O₂ concentration (1-11 mM), and pH value (2-10). The optimization yielded the highest removal efficiency of 91.95% under the following conditions: initial dye concentration of 180 mg/dm³, OAK-nZVI dosage of 60 mg/dm³, H₂O₂ concentration of 11 mM, and pH = 2.

Treatment of real effluent under optimized experimental conditions resulted in 84.06% Magenta removal after a reaction time of 60 min [93].

Considers the issues of using extracts from oak bark (*Quercus ruber*) for wastewater treatment from Cr(VI) ions are considered. The extracts were obtained by leaching sawdust with distilled water and an aqueous alkali solution by boiling for 1 hour at a ratio of 1:10, respectively, for the complete extraction of the organic component into the aqueous medium. The principle of purification is the formation of aggregates, formed by the contact of organic colloidal compounds (tannins) with positively charged heavy metal ions. It is established that the maximum formation of a precipitate is observed in acid media (pH = 2.5) [94]. This paper investigated the reagent properties of aqueous extracts from crushed oak bark sawdust to copper ions. For the experiment, the bark was pre-mechanically activated. Purification with extracts was carried out with model solutions with the concentration of ions $\text{Cu}^{2+} = 164.3 \text{ mg/dm}^3$ at pH = 2.5; 4.0; 6.0, and 9.0 to determine the most efficient removal of copper ions. The purification process was tested at different ratios of the volume of the model solution and oak bark extracts. It was found that the highest degree of removal of Cu^{2+} ions is observed at the ratio solution: extract = 1:1 at pH = 9 [95].

Alkali immersion of oak acorn (*Quercus suber*), sorghum, and potato has permitted a good purification and separation of starch granules from the matrix and allowed an extraction content of about 25%. The extracted starch showed a low capacity for water absorption and no solubility in water at room temperature, which makes it a good adsorbent and facilitates its recovery. The dye adsorption study on starch showed that the adsorption capacity content was 12.67 mg/g for oak acorn starch according to the empirical model of Langmuir [96].

7. Conclusions

The paper summarizes literature data on the use of waste (sawdust, shavings) and biomass components (leaves, bark, acorns) of *Quercus* trees and the extracts from the above components to remove metal ions (Cd^{2+} , Cr(III), Cr(VI), Cs^+ , Cu^{2+} , Fe^{2+} , Hg^{2+} , Ni^{2+} , Pb^{2+} , and Zn^{2+}) and various dyes from aqueous media. It provides brief information about the composition of *Quercus* trees components. It gives the adsorption process parameters and the values of sorption parameters for the studied pollutants. It was shown that oaks waste and biomass components' sorption characteristics for various pollutants could be increased by chemical modification with various chemical reagents. It was found that most adsorption isotherms are most accurately described by the Langmuir model and less often by the Freundlich model. The process kinetics mainly follows the pseudo-second-order model.

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Conflicts of Interest

The authors declare no conflict of interest.

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