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World Experience in Using Pine Cones to Remove Various Pollutants from Aquatic Environments

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Abstract: The paper is the first initiative to summarize literature data on the use of biomass of Pinus trees (*brutia*, *elliottii*, *halepensis*, *kesiya*, *koraiénsis*, *nigra*, *patula*, *pinea*, *radiate*, *resinosa*, *roxburghii*, *sylvestris*) cones as sorption materials to remove metal ions (As(III), Ca^{2+}, Cd^{2+}, Co^{2+}, Cr(III) and Cr(VI), Cs^{+}, Cu^{2+}, Fe^{2+}, and Fe^{3+}, Mg^{2+}, Ni^{2+}, Pb^{2+} Zn^{2+}) and various dyes from simulated and industrial wastewater. It provides brief information on the morphology of the above Pinus trees. The work has proved that the sorption capacity of various species of pine cones for metal ions and dyes can be improved by treatment with various chemicals. It was found that in most cases, the adsorption isotherms are more accurately described by the Langmuir model, and the kinetics of the process most often correspond to the pseudo-second-order model. It was found that, in most cases, the adsorption process has a physical nature.

Keywords: *Pinus*; pine cones; metal ions; dyes; adsorption; models of adsorption isotherms; thermodynamic parameters.

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1. Introduction

Chemical compound pollution in the world's oceans is frighteningly high. The main sources of pollutants entering aquatic environments are poorly treated wastewater, man-made accidents, and drains from various industrial facilities. Various methods are used to remove or decompose chemical compounds in aqueous media.

Of particular importance among the methods used is adsorption, which allows the removal of pollutants, in particular, from water of any concentration to almost zero residual values. Nevertheless, although having a high sorption activity for numerous contaminants, the activated carbons now in use have a serious drawback, i.e., their cost, which increases the cost of aqueous media treatment. Activated carbon regeneration, however, results in an increase in the economic performance of the process.

Currently, an alternative environmental safety area is rapidly developing on a worldwide scale, i.e., the use of industrial and agricultural waste, as well as wood biomass components as sorption materials to remove pollutants from aquatic environments. Tree biomass and wood processing waste are particularly interesting as sorption materials due to their accessibility, low cost, high efficiency, wide distribution area, and other valuable characteristics.

There is a wealth of international publications on the use of wood waste and wood biomass components as sorption materials. Thus, it was shown that bark [1-3], leaves [4-10], needles [11], fruit [12-16] and stones [17-19] shells, and fruit shells [20-24] are good materials to remove various pollutants from aquatic environments. Additionally, certain woody biomass components—like oak acorns, for example—have been researched as sorbents. [25]. Sawdust from during the sawing of tree trunks also showed good sorption characteristics for various pollutants [26-28].

Conifer cones are also among woody biomass components [29]. The structure of conifer cones and their morphological features are given, in particular, in Sahin *et al*. [30].

The latter has been widely studied as sorption materials to remove organic and inorganic compounds from aqueous media. However, no review papers exist on using tree cones as pollutant sorbents in international literature. This review aims to summarize the publications of Russian and foreign researchers in the above area and to assess the possibilities and prospects of using cones as sorption materials.

As shown by the literature review, the largest number of publications is devoted to studying pine cones (*Pinus*) as sorption materials.

2. The Use of Pinus Cone Biomass as Sorption Materials

Pínus is a type genus of coniferous trees, shrubs, or plantain trees of the pine (*Pinaceae*) family. Pine is one of the most widespread trees on the planet, although it is inferior to larch in terms of abundance (number of trees) and forest area with a predominance in the stand. In terms of the total area of its range, pine ranks first among coniferous trees worldwide. Pines are plants with strictly whorled branching and shoots of two types, long and short. The needles are located on the short shoots only. According to the number of needles on the short shoot, pines are divided into two-needle, three-needle, and five-needle ones. Based on current data, there are about 130 species of pine, which, in their natural growth, are scattered throughout the northern hemisphere from the equator to the Arctic, as well as in southern Africa and Australia. In temperate and subarctic climates, they grow in forests, both on the plains and in the mountains, and in the subtropics, tropics, and near the equator, they grow mainly in the mountains but also on the plains. The cones are ovate or oblong, usually drooping, falling off completely at maturity. They consist of imbricate fruit scales, woody or leathery, thickened at the end in the form of a faceted shield. These scales are tightly closed at first, but at full maturity, they open, exposing the seeds, which are 2 against each scale. Most seeds have wings, though they don't always have them, and they have a hard nut-shaped shell. There may be from 4 to 15 cotyledons in the corcule [31].

Information on the use of pine cones as sorbents will be further given in alphabetical order.

2.1. The use of Calabrian pine (Pinus brutia) cones to remove pollutants from aquatic environments.

Calabrian pine is a tree with an open crown, reaching 25-35 m in height. The bark in the lower part of the trunk is thick-scaled, red-brown, above - red-orange, thin, and flocculated cracking. The buds are narrowly ovoid, with red-brown scales covered with whitish pubescence. The needles persist for 2-4 years. Each fascicle contains two needles, 10–18 cm long, first gray-green, then bright green or yellow-green, with jagged edges. The ovules are symmetrical, turbinate, up to 12 cm long and up to 5 cm wide, green, turning red-brown after 2 years and, in the same year or after another 1-2 years, opening up to 5-8 cm. The scales are very hard, wide, and woody. The typical variety of Calabrian pine is spread from the south of the Balkan Peninsula in the north to Lebanon in the south. The Eldar pine (*P. brutia var. eldarica*) distribution area stretches from Transcaucasia to Iran [32].

We have found several literature sources on using *Pinus brutia* cone powder to remove metal ions and metalloids from aqueous media. In particular, Iranian researchers studied the adsorption of Cr(VI) ions by Calabrian pine powder. The results showed that the adsorption of Cr(VI) ions significantly depends on the pH of the solution. The maximum adsorption rate of chromium ions was achieved in the pH = 3. The maximum removal efficiency of Cr(VI) ions was 96,5 % for pine fruit powder. According to the obtained results, the adsorption of soluble chromium ions was fitted to the Langmuir isotherm model [33].

Researchers have developed a novel material by chemically modifying pine cones with isopropylidene malonate to introduce carboxylate groups. Analysis of the resulting material's adsorption properties demonstrates that its behavior aligns well with the Langmuir isotherm model at a temperature of 298 K and a pH of 4.8., and 0.4 g/dm^3 of the adsorbent, the maximum adsorption capacity of 400.0 mg/g is obtainedThe significant capacity of the material to adsorb lead ions (Pb^{2+}) is due to the presence of numerous functional groups within its structure. Furthermore, pine cones modified with carboxylate groups can be effectively regenerated and reused for lead ion adsorption for up to three cycles when employing EDTA-2Na as the elution solvent. [34].

Also, Calabrian pine cones were used as solid adsorbents for the removal of Cu^{2+} and Fe^{2+} ions from aqueous solutions through batch equilibrium technique. 90 minutes of adsorption time was found sufficient to reach equilibrium for Fe^{2+} ions and 120 minutes for Cu^{2+} ions. The results indicate that the optimum pH for the removal of Fe2+ ions was found to be pH = 5.0, and that of Cu^{2+} was pH = 7.0. The highest adsorption capacity was found to be 4.8 mg/g and 14.1 mg/g at an initial concentration of 22.22 mg/dm^3 and 57.6 mg/dm^3 of Fe^{2+} and Cu^{2+} ions, respectively. Fe^{2+} ions were removed by 96.3-97.3% and Cu^{2+} ions by 94.1-96% along the whole range of initial concentrations. Isotherm studies showed that the data best fit the Freundlich isotherm model. The kinetic data corresponded well with the pseudo-second-order equation [35].

Some more publications are dedicated to removing dyes from aqueous solutions using native and treated *Pinus brutia* cones. This study specifically examines the ability of untreated Calabrian pine cone shells to remove Basic Red 46 dye, a representative azo dye, from water. Under optimal conditions, the pine cone shell exhibited a projected dye absorption capacity of 71.77 milligrams per gram. Langmuir model fitted better to the biosorption equilibrium data (R^2=0.9782) than the Freundlich model. This displayed the monolayer coverage of dye molecules on the biosorbent surface. Dubinin-Radushkevich model and ΔG^o energy change presented that the predominant mechanism of dye biosorption by the cone shell was likely physical biosorption [36]. Kinetic data were best described by the pseudo-second-order model. The thermodynamic studies indicated that the biosorption reactions were spontaneous and endothermic. The activation energy was calculated as 32.33 kJ/mol. The Basic Red 46 dye was desorbed from the pine cones with 0.1 M HCl solution. The recovery for the dye was found to be higher than 90% [37, 38]. The maximum sorption capacity of Calabrian pine cones treated with 0.1 M NaOH increased to 89.76 mg/g [39].

Also, the cone biomass of Pinus brutia has been utilized as an adsorbent to remove Congo red dye from an aqueous solution. Maximum biosorption capacity was 102.8 mg/g. Experimental data showed that the adsorption process followed a Sips model. Experimental data shows that the adsorption of Congo red dye could be described by a pseudo-second-order equation and that intraparticle diffusion was not the only rate-limiting mechanism for the biosorption of dye. 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.

Crushed cones of Calabrian pine were studied for Acid yellow 36 dye sorption. It was found that the maximum sorption (100 mg/g) was observed at pH = 5.0, sorption material content 0.7 $g/^{dm3}$, and contact time of 20 minutes at an initial dye concentration of 10 mg/dm^3. The Langmuir model ($R^2 = 0.99$) was best suited for describing the adsorption isotherm [41].

The ability of the pine cone of *Pinus brutia* for Lanasol Yellow 2R dye removal from aqueous media was studied. The equilibrium isotherms were well represented by the Freundlich model. The maximum adsorption capacity of the pine cones for dye was found to be 41.15 mg/g. The adsorption kinetics followed the pseudo-second-order model. The thermodynamic tests revealed that the adsorption was a spontaneous and endothermic process [42].

Also, removing Methyl green dye from aqueous solutions using acid- or alkali-treated *Pinus brutia* cones (PBH and PBN) waste was investigated. Adsorption removal of dye was conducted at pH=4.5 for PBH and pH~4.8 for PBN. The pseudo-second-order model appeared to be the most appropriate for describing the adsorption process of Methylene green dye on both PBN and PBH, with a correlation coefficient $R^2 > 0.999$. The Langmuir isotherm was found to be the most relevant in describing dye sorption onto modified Calabrian brutia cones with a correlation factor $R^2 > 0.999$. The ionic strength (presence of other ions: Cl^-, Na^+, and SO_4^{2-}) also influences the adsorption due to the change in the surface properties.

The study revealed a substantial decrease (68.5%) in the adsorption capacity of Poly(brilliant heliantine blue) [PBH] when exposed to an equilibrium dye concentration of 30 mg/dm^3. Conversely, Poly(Brilliant Nile Blue) [PBN] demonstrated resilience to ionic strength variations, particularly in the presence of NaCl, with minimal impact on adsorption observed for dye concentrations exceeding 120 mg/dm^3. [43].

In Mahmoodi *et al*. [44], the adsorption of Acid Black 26 (AB26), Acid Green 25 (AG25), and Acid Blue 7 (AB7) dyes onto Calabrian pine cone was investigated in an aqueous solution. The results indicated that the isotherm data of AB26 and AG25 followed Langmuir isotherm, and the isotherm data of AB7 followed Freundlich isotherm models. It was found that the maximum sorption capacities of the dyes were 62.9 mg/g for AB26, 43.3 mg/g for AG25, and 37.4 mg/g for AB7. The study found that the experimental results for dye adsorption closely aligned with a pseudo-second-order kinetic model. Thermodynamic analysis revealed that the adsorption process is endothermic. Dye desorption studies in an aqueous solution at pH = 12 showed that maximum desorption of 93%, 97%, and 94.5% was achieved for AB26, AG25, and AB7, respectively [44].

2.2. The use of Aleppo pine (Pinus halepensis) cones to remove pollutants from aquatic environments.

Aleppo pine (*Pīnus halepēnsis*) is a coniferous tree, a species of the genus Pine (*Pinus*) of the Pine (*Pinaceae*) family. It grows in the western and northern Mediterranean. It grows in the coastal zone in small forests along slopes and dunes. In Africa, it rises in the mountains to a height of 1,750 m. The tree is 10-20 m tall and has a straight or curved trunk and strong, spreading branches. Young trees have a pyramidal crown, and old ones are wide, spreading, or umbrella-shaped. The shoots are thin, light grayish-green, glabrous. The bark is grey, turning reddish-brown later, shallowly furrowed. The needles are dark green, two per fascicle, up to 10 cm long, thin, 0.75 mm wide, soft, and persist for up to two years. The cones are 8-10 cm long, on elongated petioles, facing downwards, oblong-conical, reddish, glossy, solitary, rarely growing in two or three; the shield of fruiting scales is convex, with a prominent tip. The seeds are blackish, 6-7 mm long, with a wing up to 2.5 cm long. One kg contains up to 55 thousand seeds [45].

Some physico-mechanical and physico-chemical parameters of crushed cones of Aleppo pine are given in Almendros *et al*. [46]. It was determined that the moisture content of cones was 7.90%, volatile matter content – 74.85%, fixed carbon – 16.74%, and ashes – 0.53%. Also, the contents in lignin and holocellulose were 36.03% and 48.67%, respectively. Values of real and apparent density of pine cones were 1.441 and 0.275 g/cm^3, respectively. The content of chemical elements was: C – 46.81%, H – 7.44%, N – 0.27%, S –<0.1% and O – 45.43%. IR spectroscopy revealed the presence of the following functional groupings in the cones: O-H, C-H, C=O, C-N and N-H, C-O, C-N, and others [46]. In addition, it was determined that the surface area of the crushed cones is 0.647 m^2/g, the total pore volume is 1.344 cm^3/g, and the average pore diameter was 4.54 nm [47].

Aleppo pine cone powder was studied as a sorption material to remove heavy metal ions from aqueous media. In particular, Cu^{2+} ions adsorption by *Pinus halepensis* cone biomass under static conditions was studied. It was found that equilibrium data agreed well with the Langmuir isotherm model. The biosorption capacities of pine cones for Cu^{2+} were determined at 25.8 °C with the Langmuir model as 6.81 mg/g. The kinetics data fitted well into the pseudo-second-order model (R^2 > o.99) [47]. Ouafi *et al*., highlight that the maximum sorption capacity of cones was 9.08 mg/g. It was found that the highest sorption capacity is provided at pH = 5.5. Adsorption was also found to be spontaneous and endothermic [48]. Experiments under dynamic conditions showed that the maximum sorption capacity of 3.26 mg/g was reached at an initial concentration of Cu^{2+} ions of 100 mg/dm^3 [49].

Ni $^{2+}$ ions were removed from simulated solutions by *Pinus halepensis* cone biomass under dynamic conditions. The maximum sorption capacity was found to depend on many parameters, including the mass of the sorption material in the column. Thus, at an initial Ni^{2+} ions concentration of 100 mg/dm^3 and a sorbent content of 15 g at a volumetric velocity of 6 cm^3/min, the maximum sorption capacity was more than 5.38 mg/g [46]. Aleppo pine cones saturated with Ni^{2+} ions are proposed to be disposed of by burning [50]. Besides, it was shown that the nickel remains mainly in the ashes. Therefore, the nickel content in these ashes may be recovered or ashes distributed to any subsequent application.

Two or more metal ions adsorption by *Pinus halepensis* cone biomass was also studied, which makes it possible to compare sorption characteristics by conducting experiments under adequate conditions [51-57]. In particular, the sorption process to remove Cr(VI) and Cu^{2+} ions from simulated solutions by Aleppo pine cones and needles biomass was studied. The

Langmuir model predicted a maximum adsorption capacity of 27.78 mg/g of Cu^{2+} ions on pine cones and 64.04 mg/g of Cr(VI) ions on pine leaves. The kinetic study revealed that the pseudo-second-order model fitted the experimental data. The thermodynamic study showed that the biosorption process was endothermic for Cu^{2+} and exothermic for Cr(VI) ions. The biosorbent can be reactivated with 0.1 mol/dm^3 HNO_3 [52].

The sorption characteristics for these ions were improved by treating the cone biomass. Thus, novel biocomposite sorbent magnetic pine cone gel beads were synthesized and investigated for the single and simultaneous removal of Cu^{2+} and Cr(VI) ions from an aqueous solution. Pine cones were first magnetized with Fe_3O_4 nanoparticles and then were encapsulated in calcium gel beads. The analysis of reaction rates indicated a strong agreement with the pseudo-second-order model. Furthermore, equilibrium data fit the Langmuir isotherm model, revealing maximum adsorption capacities of 68.64 mg/g for Cu2+ ions and 212.22 mg/g for Cr(VI) ions. In systems containing multiple components, both competitive interactions and synergistic effects were observed. [53].

In Matouq *et al*. [54], low-cost local plants (eucalyptus bark, moringa pods, and pine cones) have been successfully used to remove Cr(VI) and Ni^{2+} ions from simulated wastewater with a concentration of 400, 600, and 900 ppm. The results show that moringa pods have the best removal capacity for heavy metals, with 90–99% percentages for both metals. The removal capacity percentages reach 50–98% for the eucalyptus bark, while for the pine cones, a lower removal capacity with percentages of 40-99%. The data has been best fitted to the Langmuir adsorption model for all plants. The kinetic study has revealed that the first-order kinetic model successfully describes the kinetics of Ni^{2+} ions adsorption, while the second-order describes the kinetics of Cr(VI) ions adsorption [54].

Also, the biosorption of Cu^{2+} ions in the presence of Pb^{2+} ions by native *Pinus halepensis* cone shells was investigated in batch and packed bed reactors. The behavior of competitive Cu^{2+} and Pb^{2+} ions biosorption in the batch was successfully described by the multicomponent Sips model, obtaining maximum capacities for Cu^{2+} and Pb^{2+} of 6.52 mg/g and 17.41 mg/g, respectively. Experiments conducted in a packed-bed column demonstrated that the biosorption capacity of pine cone shells for Pb^{2+} ions was significantly greater (17.85 mg/g) than for Cu^{2+} ions (9.38 mg/g). This finding reaffirms the preferential binding affinity of pine cone shells for lead ions over copper ions, even in a continuous flow system. Desorption studies indicated that Cu and Pb-loaded pine cone shells could be easily eluted by 0.3 M HCl [55].

In Amar *et al*. [56] study the effect of the contact time, pH, amount of adsorbent, and initial metal concentration in the adsorption is studied, resulting in removal percentages for Cd^{2+}, Cu^{2+}, Pb^{2+}, and Cr(VI) ions (metal concentration of 5 mg/dm^3) of 82.24%, 93.71%, 94.67%, and 88.8%, respectively (pH = 5.4, 2 g/dm^3 of adsorbent), except for Cr(VI) (pH = 2, 10 g/dm^3). The equilibrium data of Pb^{2+} and Cd^{2+} ions were found to follow the Langmuir-Freundlich model, with maximum adsorption capacities of 100.01 and 78.73 mg/g, respectively, whereas Cu^{2+} ions followed the Langmuir model with 33.55 mg/g. Cr(VI) ions adsorption data also fitted the Langmuir model, and the maximum adsorption capacity was 57.36 mg/g. Adsorption data was obtained at pH = 5.4 for divalent metal ions and at pH = 2 for Cr(VI) ions and in a range of metal concentrations ranging from 1 to 500 mg/dm^3 at 298.2 K [56].

Also, 4 types of low-cost adsorbents (Moringa pods, Eucalyptus bark, pine cones, and olive cake) were examined to remove Cd^{2+}, Cr(VI), Cu^{2+}, and Ni^{2+} ions from model waters.

The kinetic tests for pine cones demonstrated that the biosorption equilibrium is reached within 40 min for Cu^{2+} ions, 30 min for Ni^{2+} ions, and 40 min for Cr(VI) ions. The removal of Ni^{2+} and Cr(VI) ions with pine cones was tested at heavy metal concentrations of 400, 600, and 900 ppm. By using pine cones, the removal efficiencies were 43–52% for Cr(VI) ions and 72–80% for Ni^{2+} ions. When pine cones and Eucalyptus bark are used to remove Ni^{2+} and Cr(VI) ions, there is a good removal from the solution with a higher initial concentration compared with olive cake and Moringa pods. In the case of all four biosorbents, the adsorption behavior of the tested heavy metal ions could be well described using the Langmuir and Freundlich isotherm models. The adsorption kinetics showed good agreement with first- or second-order kinetics depending on the ions and biosorbents used. It could be shown that with all tested biosorbents and heavy metal ions, removal from the wastewater up to 99% was possible [57].

There are also several articles devoted to the study of dye adsorption by *Pinus halepensis* cones. Thus, the adsorption of Methylene blue dye onto pine cones was investigated. The adsorption data follow the Langmuir isotherm model. Maximum adsorption capacity was calculated at 125 mg/g. It was determined that the pseudo-second-order model was the best choice among all the available kinetic models to describe the adsorption behavior. E_a was found to be 19.57 kJ/mol. This confirms the fact that the adsorption was a physical process. The negative free energy values indicate the feasibility of the adsorption process and its spontaneous nature [58].

Native Aleppo pine cone biomass was also used to remove the Crystal violet dye from simulated solutions. It was revealed that the Langmuir model described the resulting adsorption isotherms more accurately. The maximum sorption capacity for the dye was 80.84 mg/g with the following parameters: pH = 7.0, contact time – 80 minutes, sorbent content – 0.05 g, initial dye concentration – 10-70 mg/dm^3. The kinetics of the process are more accurately described by the pseudo-second-order model [59].

A mathematical model equation was derived to determine the effect of initial pH, contact time, and initial dye concentration for the adsorption of Basic Blue 3 dye on modified pine cow with citric acid. The dye dosage was 50-300 ppm. It was determined that the pH value that provided the highest dye removal degree was pH = 7.5. It was determined that the kinetics of the process correspond to the pseudo-second-order model [60].

2.3. The use of Khasi pine (Pinus kesiya) cones to remove pollutants from aquatic environments.

Three-needled pine, Khasi pine, or Keziah (*Pinus kesiya*), is a species of evergreen coniferous tree of the genus Pine, one of the most widespread species of pines in Southeast Asia. The trees are up to 30 m high; trunk up to 60 cm in diameter; bark with deep longitudinal cracks, dark brown, peeling; crown wide domed; branches yellowish-brown in color, turning orange-brown with age. The needles are arranged 3 pcs per fascicle, are thin, flexible, 10-22 cm long, and triangular in cross-section (0.7-1 mm). Cones are single or paired, egg-shaped, sized 5.5 by 3.5 cm. The seeds are black-brown, slightly oblate, elliptical, sized 5-6 by 3-4 mm. The tree is also known as *Pinus insularis* [61].

There is virtually no information in the literature on the study of Khasi pine cones as a sorption material. In particular, the batch adsorption of Pb^{2+} and Cu^{2+} in separate mono systems was studied using powdered *Pinus* insularis cone. A full factorial 23 factorial design was employed for this. This study also aimed to simulate the continuous adsorption of Pb^{2+} and Cu^{2+} ions using Aspen Adsorption® Version 8.4. The initial concentrations of metal ions were

20-200 ppm. It was found that both isotherms were more accurately described by the Langmuir model. The maximum sorption capacities for Cu^{2+} ions were 9.98 mg/g, for Pb^{2+} ions - 10.04 mg/g. Comparable sorption capacity values were also obtained through experiments under dynamic conditions [62].

2.4. Using Korean pine (Pinus koraiénsis) cones to remove pollutants from aquatic environments.

Korean pine (*Pínus koraiénsis*) is a coniferous tree, one of the genus Pine species, native to east Asia, northeast China, Primorsky and Khabarovsk Territories, southeast Amur region, Korea, and central Japan. This tree is up to 40-50 m tall, can reach 1.5-2 m in diameter, and the volume of the trunk wood is up to 15-17 m³. The bark is brown-gray with a reddish tinge, flaky, rather thin. The crown is developed, dense, cone-shaped, or rounded-ovate in young trees, oblong-cylindrical or obovate in old age. The trees are wind-resistant. Over the years, they require more light and fresh, fertile soil, but not waterlogged. The young shoots are thin, and densely pubescent with red hairs. Cedar needles are bluish-green, triangular, long (7-20 cm), 1-1.5 mm wide, with rough-serrated ribs. The needles are grouped in fascicles by five and persist for two to four years on the branches.

The plant is monoecious. Staminate strobiles are yellow, and female cones are reddish-purple. Cones ripen at the end of August - October the next year after "flowering"; they are large, up to 17 cm long, up to 8 cm wide and more, elongated-ovoid, and do not open when ripe. As a rule, after ripening in autumn or early winter, they fall off together with the seeds. Each cone contains many nuts; the seeds are obovate, 14-18 mm long and 8-10 mm wide, with a thick woody coat, wingless, various in shapes and sizes. One tree can produce about 500 cones; an average cone size is 130 to 150 nuts [63].

Several articles have been found in the world literature on using *Pínus koraiénsis* cone biomass to remove heavy metal ions from aqueous media. In particular, the studies include the adsorption interaction of crushed treated Korean pine cones with Cd^{2+} ions. Pine cones treated with H_2SO_4 were tested to remove Cd^{2+} ions from aquatic environments. The results showed the Cd^{2+} ions adsorption capacities of the native pine cones powder and modified pine cones were 14.96 and 74.94 mg/g, respectively. The equilibrium adsorption data are more consistent with the Langmuir isotherm equation than the Freundlich equation. The optimum pH for Cd^{2+} adsorption is pH = 6.0. The desorption ability of Cd^{2+} ions by 0.1 M HCl solution was found to be around 96.7- 99.1% [64].

Reports potential application of Korean pine cones and its acids treated as adsorbents for removal of Pb^{2+} ions in water. Two different types of acids were used for the treatment of pine cones at different activation temperatures, with the following combination of HCl-treated cones at 25°C (PC-H25) and 50 ◦C (PC-H50); H_3PO_4 treatment PC at 25°C (PC-P25) and 50°C (PC-P50). It was estimated through adsorption isotherm analysis that the adsorption capacities of PC-H25, PC-P25, PC-H50, and PC-P50 on Pb^{2+} ions were 132.6, 108.2, 148.3, and 119.8mg/g, respectively. Desorption studies revealed the promising regeneration potential of pine cone biomass. It was found that the removal of Pb^{2+} ions was maintained at more than 60% as compared to the initial value, even after 5 adsorption-desorption cycles [65].

In Kim *et al*. [66], biosorbents to remove Cd^{2+} and Pb^{2+} ions included, in particular, tree biomass components. Forest biowastes used in this study were bark, chestnut bur, sawdust, Korean pine cone, pine needle, and pine-nut cone. It was found that an increase in pH values resulted in an increase in the sorption capacity for these metal ions. It was determined that the resulting sorption capacities for Cd^{2+} ions were (mg/g): pine cone – 4.29, pine needle – 6.65, and pine-nut cone – 10.92. For Pb^{2+} ions, the sorption capacities were 15.17, 25.86, and 27.16 mg/g, respectively. Langmuir model could fit the equilibrium isotherm data better than the Freundlich model. The pseudo-second-order equation satisfactorily described the biosorption behaviors of both metals. The biosorption rate of Pb^{2+} ions was 3.12 times higher than that of Cd^{2+} ions. FTIR study showed that the carboxyl group on the biosorbent was involved in biosorbing the metal ions [66].

2.5. The use of the Black pine (Pinus nigra) cones to remove pollutants from aquatic environments.

We have found several literature sources on the use of crushed black pine (*Pinus nigra*) cones biomass as a sorption material to remove pollutants from aquatic environments.

Black pine (*Pinus nigra*) is a coniferous tree, a species of the genus Pine (*Pinus*) of the Pine (*Pinaceae*) family. The habitat, for the most part, is the northern Mediterranean; there are several areas in Morocco and Algeria. It rises in the mountains to a height of 1,400-1,500 meters. The tree is 20-55 m tall, with a pyramidal crown for young and an umbrella-shaped crown for old trees. The branches at the end are more or less ascending. Annual shoots are gray-brown. The bark is black-gray and deeply striated. The age of the trees reaches 600-800 years. Needles 8-14 cm long, 1.6-1.8 mm wide, dark green, slightly shiny or matte, two pieces in a fascicle, hard, pointed, straight or slightly bent, often twisted. Cones are ovate or somewhat elongated, 5-7.5 cm long, 2-3.5 cm wide, yellow-brown, shiny gray-brown, on short petioles, arranged horizontally on branches, open in the third year [67].

A study was conducted on using black pine cone biomass treated with citric acid as an ion exchanger to remove Cu^{2+} ions under dynamic conditions. The initial concentrations of Cu^{2+} ions were 100-1000 mg/dm^3, and the volume of the passed solution was 25 cm^3 at a rate of 3.3 cm^3/min. It was determined that the efficiency of copper ion removal depends on the initial concentration, and at an initial concentration of 100 mg/dm ^{3} is 80.4%, and at a concentration of 1000 mg/dm^3 – 77.6% [68].

Pinus nigra cones treated with citric acid have also been studied as a cation exchanger to remove hardness ions under dynamic conditions. It was found that with an initial aggregate Ca^{2+} and Mg^{2+} ion content of 385 mg/dm^3, pine cone weight of 10 g, the volume of passing water 100 cm^3 at a rate of 3.3 cm^3/min, the efficiency of hardness ion removal was more than 80% when using native cones – 10% [69].

Argun *et al.* [70] describe the activation of pine cones with a Fenton reagent and determine the removal of Cd^{2+} and Pb^{2+} ions from an aqueous solution. Different adsorption isotherms were also obtained using concentrations of heavy metal ions ranging from 0.1 to 150 mg/dm^3. The adsorption process follows pseudo-first-order reaction kinetics and follows the Langmuir adsorption isotherm. Revealed that the adsorption process was spontaneous and exothermic under natural conditions. The maximum removal efficiencies were obtained as 91% and 89% at pH = 7 with 90 and 105-min contact time for Cd^{2+} and Pb^{2+} ions, respectively [70].

In addition, Anatolian black pine (*Pinus nigra* Arnold.) was evaluated as a biosorbent for the removal of Crystal violet dye from aquatic solution. The influence of operational parameters, including solution pH, initial dye concentration, biosorbent dosage, contact time, and temperature, were studied in batch systems. The adsorption data followed well Langmuir isotherm with a maximum biosorption capacity of 12.36 mg/g. The equilibrium data were better fitted with the pseudo-second-order kinetic model ($R^2 > 0.99$). The thermodynamic parameters indicated that the Crystal violet biosorption was a feasible, spontaneous, and endothermic process [71].

2.6. The use of the spreading-leaved pine (Pinus patula) cones to remove pollutants from aquatic environments.

The spreading-leaved pine (*Pínus patula*) is a plant species of the genus Pine (*Pinus*) of the Pine family (*Pinaceae*). The species has been introduced to coastal areas of New South Wales, Australia. Its natural dispersal via wind and the region's ample summer rainfall have facilitated its proliferation. It was also introduced in New Zealand for commercial purposes and is fully naturalized there. The tree is 20-25 meters high. The trunk often branches into two or more leading shoots at a low height. The branches are long, relatively thin, and spreading. The bark of the trunk is red-brown lamellar. Needles are arranged in a fascicle by 3, sometimes by 4 and 5, light green hanging or spreading, thin, dense, 15-22 cm long, and 1 mm wide. Cones are matte-light brown, 7-10 cm long, arranged in whorls by 2-5, ovate-conical, asymmetrical. The petioles are short. The seeds are 0.5 cm long, triangular, gray with black spots. The wing is 2.2-1.8 cm long [72, 73].

The *Pinus patula* cone biomass has been extensively studied as a sorption material to remove contaminants from aquatic environments. Most publications are devoted to the removal of metal and metalloid ions from simulated and natural wastewater. Thus, *Pinus patula* cone biomass was chemically activated with NaOH and applied as a potential adsorbent for As(III) ions in water. It was found that the Langmuir model more accurately describes the adsorption isotherms, and the kinetics of the process correspond to the pseudo-second-order model. The values of the maximum sorption capacity were 14.83-22.33 mg/g in the temperature range 299-319 K. Temperature effect on adsorption kinetics and equilibrium studies indicates ligand exchange as the main sorption mechanism with an activation energy of 26.24 kJ/mol. The results showed that As(III) ions inhibition increased with pH, and among the anions, PO_4^{3-} anions inhibited As(III) ions adsorption strongly while As(III) ions uptake was slightly increased in the presence of CO_3^{2-}, SO_4^{2-} and Cl^- anions [74].

Also, magnetite-coated pine cone biomass was synthesized and characterized, and its interaction with As(III) ions in water was evaluated to apply it as an efficient adsorbent. Adsorption studies showed that the optimum pH of As(III) ions adsorption was pH = 8 and that Fe^{3+} ions leaching was negligible at this pH. The optimum Fe_3O_4:pine cone ratio for As(III) ions removal was 2.0:1.5 with an adsorption capacity of 13.86 mg/g. The pseudo-second-order model best fitted the kinetic data with an activation energy of adsorption, which was calculated to be 23.78 kJ/mol. The Langmuir isotherm described the equilibrium data best, while the values of Dubinin–Radushkevich mean free energy suggest an anion-exchange process [75].

Increasing ionic strength slightly increased the As(III) ions capacity of magnetite-coated pine cone from 13.86 to 17.82 mg/g at optimum solution pH = 8, but As(III) ions adsorption was reduced by PO_4^{3-} anions and humic acid due to competition [76]. Spectroscopic evidence confirmed ion exchange through the observance of hydroxyl peak shift, reduction in the intensity of carboxylate peaks, and As-O-Fe bond formation during adsorption. Also, results confirmed that there was a simultaneous reduction of Fe^{3+} to Fe^{2+}, oxidation of arsenite to arsenate, and adsorption of both arsenite and arsenate on the composite surface through the formation of inner-sphere complexes [77].

Also, magnetized pine cone powder was used to remove Cr(VI) ions from model solutions. The composite with 1.5 g of pine removed more Cr(VI) ions at all solution pH's applied, and pH = 3 was optimum, at which point Fe^{3+} leached into the solution was less than 0.01 mg/dm^3. The Langmuir monolayer capacity was observed to be 15.24 mg/g at 26°C while Dubinin–Radushkevish free energy ranged from 15.80 to 16.80 kJ/mol, suggesting ligand–ion exchange mechanism [78]. The changes in enthalpy and entropy were determined to be 78.3 kJ/mol and 323.3 J/mol·K for the prepared nanocomposite [79].

Dynamic studies were done using a breakthrough curve to evaluate the concentration effect of Cr(VI) ions adsorption. Thomas's model best described the dynamic behavior, while desorption studies showed that four adsorption-desorption and regeneration cycles were possible with an elution efficiency >87% and only a 15% loss of capacity after 4 cycles [78, 80].

A study was devoted to the adsorption of Cs^+ ions by *Pinus patula* cones treated with an ethanol-toluene mixture. It was found that cone powder treatment increases the surface area from 4.60 m^2/g to 28.60 m^2/g and the total pore volume from 0.004 cm^3/g to 0.173 cm^3/g. The experiments were carried out to test the efficiency of the sorbents for Cs^+ ions removal from aqueous solution. The Cs^+ ions adsorption capacity for raw pine cone was found to be Qe = 1.46 mg/g. On modification with a toluene–ethanol mixture, the Cs^+ ions adsorption capacity was found to be Q_e = 1.83 mg/g [81]. Increased hydrophilicity and Cs^+ ions affinity were observed for treated pine cones due to organics extraction, increased surface area, and formation of carboxylate ions, which also produced higher uptake rates for pseudo-first and second-order rate constants as compared with the raw pine cones. Diffusion–the chemisorption model better fitted the kinetic data for the treated pine cones, while the pseudo-second-order model fitted the raw pine cones [82]. Also, pine cones treated with an ethanol-toluene mixture were additionally treated with iron (III) hexacyanoferrate. The additional treatment provided an increase in the maximum sorption capacity for Cs^+ ions to 8.75 mg/g. It was found that the adsorption isotherms in all cases were more clearly described by the Langmuir model. The mechanism of Cs^+ ions adsorption onto raw pine cones followed the pseudo-second-order model and involved stripping the hydration water from the metal ion [83, 84].

Native and 0.15 mol/dm^3 NaOH solution-treated pine cones were studied for their adsorption capacity for Cu^{2+} ions. It was found that such treatment ensured an increase in maximum sorption capacity from 6.8 mg/g to 17.22 mg/g at 291 K. It was determined that an increase in the solution temperature resulted in an increase in the maximum sorption capacity. The process of modifying the surface of pine cone powder resulted in a significant decrease in the point of zero charge (pHPZC) from 7.49 to 2.55. Concurrently, this modification led to an expansion of the material's internal surface area. Cu^{2+} ions biosorption studies revealed that the optimum solution pH and biosorbent dose for Cu^{2+} ions removal was pH = 5 and 8.0 g/dm^3 for the untreated and treated samples. Biosorption temperature was found to increase Cu^{2+} ions uptake for all samples, indicating that Cu^{2+} biosorption is endothermic. Activation energy computed from the pseudo-second-order rate constant increased with NaOH modification from 18.22 to 21.39 kJ/mol. The thermodynamic parameters of activation were computed using the Erying equation, and the findings indicate that the reorientation process during activation is primarily driven by entropy. Furthermore, the study suggests that the role of entropy in this reorientation step diminishes following treatment with NaOH washes, and this effect becomes more pronounced with increasing NaOH concentrations. [85-87].

Pinus patula cone biomass was also treated with a 0.15 mol/dm^3 $Ca(OH)_2$ suspension and used to remove Cu^{2+} ions from simulated solutions at various temperatures. It is found that the kinetics of the process in both cases followed the pseudo-second-order model. The treatment helps increase the maximum sorption capacity from 6.8 mg/g to 17.85 mg/g at 291 K. The free energy of activated (ΔG°) was found to be lower for $Ca(OH)_2$ treated pine cone powder, indicating that activation is more spontaneous than for raw pine cone powder [88].

Also, the effect of different chemical activating agents (NaOH, KOH, and $Ca(OH)_2$) on external and internal diffusion of Cu^{2+} ions onto pine cones has been studied. Base treatment favored the formation of new pores with mesopore predominating in the order of raw < $Ca(OH)_2$ <KOH < NaOH treatment. The alkaline treatment helped increase the surface area of the treated samples. Thus, the native cone powder surface area was 4.39 m^2/g, while after treatment with NaOH, it boosted to 63.15 m^2/g. The total pore volume was 0.04 cm^3/g and 0.193 cm^3/g, respectively. The sorption capacities depended on the initial concentration of Cu^{2+} ions in the solution. At an initial copper ions concentration of 120 mg/dm^3, the sorption capacities were 5.76 mg/g (raw), 13.80 mg/g ($Ca(OH)_2$), 14.96 mg/g (KOH), and 16.53 mg/g (NaOH). Initial solution pH affected the removal of Cu^{2+} ions to a greater extent for the base-treated samples than for the raw pine cone [89].

This study investigates how different toluene-ethanol solvent ratios (1:1, 2:1, 1:2, and 1:3) used for modification over 8 hours affect the surface characteristics and lead ion (Pb^{2+}) adsorption behavior of pine cone powder.An amount (0.5 g) of each of the samples was contacted with 100 cm^3 of 300 mg/dm^3 Pb^{2+} ions solution adjusted to pH = 5 for 2 h at room temperature. The Pb^{2+} ions adsorption capacities (Qe, mg/g) obtained were 13.6, 16.1, 17.2, 12.8, and 14.7 mg/g for the raw, 1:1, 2:1, 1:2, and 1:3 toluene–ethanol extracted samples, respectively. It was determined that Pb^{2+} ions adsorption was inversely related to surface charge and directly related to iodine capacity. Ion-exchange was the dominating mechanism, followed by chemisorption. Shifts in peaks of FTIR spectra indicate that unbounded –OH and acidic groups were responsible for Pb^{2+} ions bonding [90].

In addition, the sorption of Pb^{2+} ions onto pine cone powder (PCP) and 0.01-0.15 mol/dm^3 NaOH treated pine cone powder was studied to evaluate the effect of NaOH treatment on the kinetics of Pb^{2+} ions uptake by performing batch kinetic sorption experiments. Equilibrium biosorption studies performed showed that the Langmuir isotherm better fit the equilibrium data for all samples, indicating that biosorption sites are homogenous regardless of surface modification. Native pine cones' maximum sorption capacity was determined at 8.46 mg/g. After 0.15 mol/dm^3 treatment, it increased to 24.71 mg/g, almost three-fold. The pseudo-second-order model best described the experimental data for the effects of biosorbent dose and initial Pb^{2+} concentration. The batch biosorption model, based on the pseudo-second-order mechanism, was applied to predict the rate constant of biosorption, the equilibrium capacity, the initial sorption rate, the effects of biosorbent dose, and the initial Pb^{2+} ions concentration [91, 92].

The kinetics of Pb^{2+} ions' adsorption onto increasing masses of raw and $Ca(OH)_2$-treated *Pinus patula* cone powder was evaluated. It was determined that the total acidic functional groups of $Ca(OH)_2$-treated pine cone were observed to decrease from 3.20 to 2.49 mmol/g as compared with the raw sample. It was determined that the isotherms of $Pb2^+$ ion adsorption by raw and treated biomass of cones are well described by the Langmuir model. The first rapid stage in the adsorption profile was found to be controlled by film and intraparticle diffusion, while the slow movement of Pb^{2+} ions influenced the second slow stage through longer diffusion paths created by particle aggregation, especially at higher doses. The results suggest that adsorption capacity decreases with increasing adsorbent dose, and

$Ca(OH)_2$-treated samples have higher capacities than the raw samples. The authors [93] have compared three multistage batch adsorber models based on the Langmuir isotherm.

Ofomaja A.E. and colleagues also studied the adsorption of two or more metal ions by *Pinus patula* cone biomass. In particular, they studied the removal of Co2+ and Ni2+ ions by pine cone powder. It was found that increasing the pH solution led to increased Co $^{2+}$ and Ni $^{2+}$ ions uptake, with Ni $^{2+}$ ions being more adsorbed. Adsorption capacities correlated well with change in solution H^+ ion concentration when solution pH = 3-8 and metal ion concentrations were varied between 5 and 150 mg/dm^3. Dubinin–Radushkevich isotherm better fitted the experimental data. It was determined that at an initial 35 mg/dm^3 metal ions concentration, the sorption capacities for Co^{2+} ions were 0.9 mg/g, and for Ni^{2+} ions - 1.2 mg/g. The affinities of the metals for functional groups on pine cone biomass depended on the ionic radius, surface precipitation complexes, and covalent bond strength. Desorption studies confirmed the ion-exchange mechanism. It was observed that Ni^{2+} ions showed stronger ion-exchange properties than Co^{2+} ions biosorption [94].

Also, pine cone powder was pretreated using a Fenton reagent and modified by grafting with acrylic acid. Furthermore, a new poly(hydroxamic acid) ligand was synthesized from the poly(acrylic acid) grafted pine cone powder for Cu^{2+} and Fe^{2+} ions removal from aqueous media. It was determined that the isotherms of adsorption for these ions by treated pine powder were more accurately described by the Langmuir model. The maximum sorption capacities calculated on the basis of the Langmuir equation were 5.08 mg/g for Cu^{2+} ions and 5.75 mg/g for Fe^{2+} ions. The theoretical values Qe of the pseudo-second-order model compared with those for the pseudo-first-order kinetic model agree with the experimental value Qe. Therefore, these results confirm the chemisorption of Cu^{2+} and Fe^{2+} ions onto poly(hydroxamic acid) ligands [95].

The pine cone powder surface was treated with NaOH and applied to remove Cu^{2+} and Pb^{2+} ions from the solution. As the solution pH increased, the biosorption capacity and the change in H^+ ion concentration in the solution increased. The change in H^+ ion concentration for Pb^{2+} biosorption was slightly higher than for Cu^{2+} biosorption. Equilibrium studies showed that the Langmuir isotherm gave a better fit for the equilibrium data, indicating monolayer coverage of the biosorbent surface. The pseudo-first-order kinetics gave a better fit. The pseudo-second-order kinetics gave a better fit to the experimental data over the temperature range from 291 to 347 K, and the equilibrium capacity increased from 15.73 to 19.22 mg/g for Cu^{2+} ions and from 23.74 to 26.27 mg/g for Pb^{2+} ions. The activation energy was higher for Pb^{2+} ions (22.40 kJ/mol) than for Cu^{2+} ions (20.36 kJ/mol). The results revealed that ion-exchange is the main mechanism for biosorption for both metal ions [96].

Mzinyane *et al*. [97] report on the adsorption purification of acid mine waters using *Pinus patula cones as an adsorbent.* The surface of the biosorbent was improved by pre-treatment using a Fenton reagent and then modified using chemical grafting of acrylic acid onto pine cone powder with free radical initiation. The modified adsorbent was used to adsorbate Cu^{2+}, Fe^{3+}, Mn^{2+}, Pb^{2+}, and Zn^{2+} ions from a single-component solution and acid mine drainage sample. The optimum pH for the poly(hydroxamic acid) ligand was pH = 6 for all heavy metal ions investigated, with the percentage removal of 79, 83, 82, 90, and 73% for Fe^{3+}, Cu^{2+}, Mn^{2+}, Zn^{2+}, and Pb^{2+} ions respectively. The adsorption of the heavy metal ions onto the ligand fitted well with the Langmuir isotherm model due to $R^2 > 0.99$. The ligand's binding capacity (Qe) with metal ions such as Fe^{3+}, Cu^{2+}, Mn(II), Zn^{2+}, and Pb^{2+} ions were 13, 14, 11, 11, and 12 mg/g, respectively. Furthermore, pseudo-second-order kinetics was the best to describe adsorption kinetics for acid mine drainage metal ions using poly(hydroxamic acid) ligand [97].

Several literature sources report the use of spreading-leaved pine cones to remove organic substances from aquatic environments. In particular, the ability of polyaniline-coated pine cones to remove Direct orange 26 dye from wastewater was investigated. It was observed that the percentage of dye removal decreased with increasing solution pH. The results also indicate that adsorption efficiency increased with an increase in temperature, which predicts that the adsorption process is endothermic. The maximum percentage of dye removal was found to be 99.98% at pH = 4.17, adsorbent dosage 0.1 g, and initial dye concentration 50 mg/dm^3. Kinetic studies revealed that equilibrium was reached within 90, 180, and 240 min of interaction for initial dye concentrations of 50 mg/dm^3, 100 mg/dm^3, and 150 mg/dm^3, respectively [98].

Also, pine cone powder was cross-linked with hexamethylene diisocyanates and applied as an adsorbent for 2-nitrophenols from an aqueous solution. Pine cone powder was pre-treated with Fenton reagent to improve surface area porosity of the adsorbent and to add carboxylic acid sites for cross-linking. Redlich-Peterson isotherm best described the adsorption process. The Langmuir maximum capacities for raw, Fenton pretreated, and Fenton pre-treated cross-linked samples were 41.17, 65.75, and 78.05 mg/g. The adsorption kinetics of 2-nitrophenol in the concentration range of 100-400 mg/dm^3 was best described by the pseudo-second-order kinetics. The adsorption mechanism for the crosslinked adsorption was found to be via p-p, polar, and hydrophobic interaction [99].

It is obvious that almost all studies on the use of *Pinus patula* cone biomass have been conducted by a scientific team led by Ofomaja A.E.

2.7. Using the stone pine (Pinus pinea) cones to remove pollutants from aquatic environments.

Stone pine, or Italian stone pine (*Pinus pinea*), is an evergreen tree from the pine family. It is naturally found on the Mediterranean coast from the Iberian Peninsula to Asia Minor. The tree is 20-30 m tall and lives up to 500 years. The crown is dense, dark green, umbrella-shaped, and compact, with horizontally spreading branches in old trees. Needles are arranged in fascicles, two pieces each, long (10-15 cm), narrow, dense, evergreen, and sometimes bluish. Cones are usually single or grouped by two to three, 8-15 cm long, ovoid, or almost spherical. The seeds ripen in the third year in October, but the cones do not open until the following spring. After the seeds fall out, the cones hang on the branches for another two to three years. The seeds are elongate-ovate, dark brown, sometimes with light spots, and have three ribs. They are 15-17 mm long and 8-9 mm wide. They have thick shells and narrow, short wings. The seeds are edible. Stone pine seeds are the largest among pines (and in the pine family in general). They are 3-4 times larger than cedar. There are 1,500 of them in one kilogram. The yield is quite high - from 3 to 8 tons of seeds per hectare [100].

The crushed pine cone biomass was studied to remove Cd^{2+}, Cr(VI), Cu^{2+}, and Pb^{2+} ions under static conditions. In this case, Pb^{2+} ions followed the Freundlich model, Cu^{2+} ions followed the Langmuir model, and Langmuir-Freundlich was the best model for Cd^{2+} and Cr(VI) ions. The efficiency of a milled pine cone in removing trace concentration levels of Pb^{2+}, Cu^{2+}, and Cd^{2+} ions has been demonstrated as resulting in capacities of 119.04 mg/g, 50.0 mg/g, and 33.55 mg/g at pH = 5.5, respectively, and 68.03 mg/g at pH = 2 for Cr(VI) ions. The kinetic data fitted well into the pseudo-second-order model. Moreover, competitive experiments using multi-metal solutions were performed. They proved the absence of competition between Pb^{2+}, Cu^{2+}, and Cd^{2+} ions on the adsorbent sites at low metal concentration levels (1-10 mg/dm3). In contrast, in the case of pine cones, the sorption capacities of metals decreased to 6.8% (30% reduction) for Cu^{2+} ions and 9.8% (15% reduction) for Cd^{2+} ions, respectively [101].

Also, the pine cone and oak cups pulp biomass were used as low-cost adsorbents for the removal of basic (Basic Red 18) and acidic (Acid Red 111) dyes and Cr(VI) ions from aqueous solutions. The adsorbents were modified by HNO_3 to improve their biosorption capacity. The modification of pine cone increased its adsorption capacity for the basic dye, whereas the modification of oak cup pulp decreased the adsorption ability for the basic dye to some extent. The adsorption isotherms fitted the Langmuir model. The adsorption capacities were found to be 142.85 and 158.73 mg/g for modified and raw pine cone biomass. The acidic dye and Cr(VI) ions adsorptions were much lower compared to basic dye on all tested adsorbents [102].

2.8. The use of Monterey pine (Pinus radiata) cones to remove pollutants from aquatic environments.

Monterey pine (*Pínus radiáta*) is a species of woody plant of the Pine (*Pinus*) genus, the Pine family (*Pinaceae*). Trees are 15-30 m tall with a trunk 30-90 cm in diameter and with a thick, wide-conical crown that grows spherical-conical, spherical, or flattened as it ages. The bark is reddish-brown, turns gray or almost black as it ages, and is furrowed between elongated rectangular scaly ridges. Young shoots are 3-4 mm thick, more or less smooth, and light brownish-yellow. Older ones are brown or gray. There are 2 needles (var. binata) or, more often, 3 in a fascicle, 9-15 cm long and slightly less than 2 mm wide. The seed cones are ovoid before opening, broadly ovoid when opened, 7-15 cm long, yellow-brown, shiny, numerous, from solitary to whorled, spreading to curved scales, rigid, and can persist for many years. The seeds are compressed-ellipsoid; the body is about 6 mm, dark brown; the wing is 20-30 mm [103].

The kinetics and mechanism of Methylene blue dye adsorption onto raw *Pinus radiata* pine cone biomass were investigated under various physicochemical parameters. Equilibrium data were best represented by Langmuir isotherm among Langmuir and Freundlich adsorption isotherm. The maximum monolayer adsorption capacity of pine cone biomass was 109.89 mg/g at 30°C. The kinetic studies showed that the dye adsorption process followed pseudo-second-order kinetics among various kinetic models tested. Thermodynamic parameters such as standard Gibbs free energy ($\Delta G° = -7.56$ kJ/mol at 30°C), standard enthalpy ($\Delta H° = -26.50$ kJ/mol), standard entropy ($\Delta S° = -62$ J/mol·K) and the activation energy ($A = -23.98$ kJ/mol at 30°C) were calculated [104]. Monterey pine cone powder treatment with NaOH provided an increase in the maximum sorption capacity to 142.86 mg/g [105, 106]. *Pinus radiate* cone biomass was also studied under dynamic conditions to remove Methylene blue. To determine the fixed-bed column adsorption kinetic parameters, Thomas, Yoon–Nelson, and Bed Depth Service Time (BDST) models fitted the experimental breakthrough curves obtained from dynamic studies. It was found that all these parameters are required for the design of the adsorption column, and all three kinetic models were applicable [107].

Pine cone has been studied for its potential application as an adsorbent in its raw and hydrochloric acid-modified form. Equilibrium data were best represented by the Freundlich isotherm model.

The study found that the effectiveness of dye adsorption onto pine cones was influenced by pH levels. Using raw pine cones, the highest amount of dye adsorbed (32.65 mg/g) was achieved at a pH of 3.55 when the initial dye concentration was 20 ppm. Treatment with acid further enhanced the adsorption capacity of the pine cones, resulting in maximum adsorption of 40.19 mg/g under the same conditions. Kinetic studies showed that the dye adsorption process followed pseudo-second-order kinetics. The thermodynamic analysis indicates that the system was endothermic and physical processes in nature [108].

The adsorption characteristics for the uptake of a ternary dye mixture of safranine O, brilliant green, and methylene blue (SO, BG, and MB) dyes by pine cone modified with β-cyclodextrin were investigated. The adsorption predominately followed the Langmuir isotherm and was controlled by physical sorption and electrostatic interactions. The maximum sorption capacities were determined to be 182.7 mg/g for SO, 158.6 for BG, and 136.7 for MB at 35° C. The adsorption process primarily followed a pseudo - second order model, and the rate of adsorption was inversely proportional to the initial dye concentration. The adsorption was also a multi-stage process that was limited by intraparticle diffusion. The adsorption was spontaneous and endothermic [109].

It was also undertaken to evaluate the adsorption potential of a pine cone (Pinus radiata) and remove sodium dodecyl sulfate from an aqueous solution. Kinetic studies showed that the surfactant adsorption process followed pseudo-second-order kinetics based on pseudo-first-order and intraparticle diffusion models. Equilibrium data were fitted by both the Langmuir isotherm and Freundlich adsorption isotherm. The maximum monolayer adsorption capacity of pine cone biomass was 95.75 mg g^{-1} at 20°C [110].

Also, pine cone biomass is used to remove dye and surfactants from their aqueous solution. The results showed that the amount of adsorption of organics depends on various physico-chemical factors such as concentration, contact time, solution pH, temperature, and the amount of adsorbent. Overall, the kinetic studies showed that the adsorption process followed pseudo-second-order kinetics, a two-step process [111].

2.9. The use of red pine (Pinus resinosa) cones to remove heavy metal ions from aquatic environments.

Norway pine or red pine (*Pinus resinosa*) is a North American plant of the Pine (*Pinus*) genus, the Pine family (*Pinaceae*). It is the symbol tree of the state of Minnesota. Red pine is up to 37 m in height, with a trunk reaching 1.5 m in diameter, with a rounded crown. The bark is reddish-brown, scaly-furrowed. Young branches are orange-brown and later darken. The needles are up to 18 cm long, arranged in fascicles usually by 2, straight, of various shades of yellow-green; the edges of the needles are toothletted. Male strobili are elliptical, about 1.5 cm long, and dark lilac. The ovules are biennial. Immature ones are ovated, then open, and become broadly ovated, red-brown in color, 3-6 cm long. The scales are rigid, with a short-pointed tip [112].

One publication has been found devoted to the study of Cu^{2+} and Pb^{2+} ion adsorptions by crushed *Pinus resinosa* cone biomass. It was observed that the adsorption was pH-dependent, and maximum adsorption was found at pH = 5.0. The adsorption capacity of the biosorbent did not change with temperature. The experimental data fit well with the Langmuir isotherm model, which shows the monolayer coverage of the biosorbent. The maximum Cu^{2+} and Pb^{2+} ions adsorption capacities of the pine cones from the Langmuir model were 21.93 mg/g and 11.72 mg/g, respectively. The kinetic studies showed that the Cu^{2+} and Pb^{2+}

adsorption processes followed a pseudo-second-order kinetic model. The biosorption process is mainly dominated by the ion exchange mechanism [113].

2.10. The use of chir pine (Pinus roxburghii) cones to remove heavy metal ions from aquatic environments.

Pinus roxburghii Sarg. is a species of several evergreen trees belonging to the *Pinaceae*. It is native to the Himalayas and is distributed throughout Pakistan, India, Nepal, and Bhutan. *Pinus roxburghii* is a large tree attaining up to 28-55 m in height with a trunk diameter reaching 2 m. The cones of *Pinus roxburghii* are ovoid conic and usually open up to 20 cm to release the seeds. *Pinus roxburghii* oil has been traditionally used to treat cuts, wounds, boils, and blisters. In addition, phytochemical screening of Pinus needles and stems has found abundant amounts of vitamin C, tannins, and alkaloids, while the stem has been primarily used as a source of turpentine oil [114].

Pollen cones grow spirally at the base of young shoots. They are ovoid-oblong in shape and 13 to 15 mm long. Seed cones grow in singles or whorls by two to five on strong twigs. They are short-stemmed, broadly ovoid or ovate-conical, 10-15, rarely 20 cm long, and 7-12 cm wide when closed. They open slightly only after a few years and have a maximum diameter of 13 cm. The seed scales are elongated, woody, and inelastic [115].

One publication on using Pinus roxburghii cones as sorption materials has been found in periodicals. Thus, in Tyagi *et al*. [116], pine forest residues such as pine needle (PN-R), pine-cone (PC-R), and pine bark (PB-R) were characterized for their physicochemical properties and then were utilized as adsorbents for the removal of Cu^{2+} ions from synthetic wastewater. All the pine residues were composed of cellulose (25-30%), hemicellulose (32-37%), and lignin (35-40%). Experiments involved varying pH (2.0–6.0), contact time (0.5–24 h), initial Cu^{2+} ions concentration (5-70 mg/dm^3), and S:L (2-8 g/dm^3). PC-R, PB-R, and PN-R were found to have maximum adsorption capacity of 11.4 mg/g, 10.45 mg/g, and 9.7 mg/g, respectively, at pH = 6.0, S:L of 2 g/dm^3, initial Cu^{2+} ions concentration of 70 mg/dm^3, and contact time of 6-8 h. Langmuir isotherm model best fitted the adsorption data for pine residues, confirming monolayer adsorption. The present study showed that pseudo-first-order best fitted the Cu^{2+} ions sorption kinetic data [116].

2.11. The use of Scots pine (Pinus sylvestris) cones to remove various contaminants from aquatic environments.

Scots pine (*Pínus sylvéstris*) is a widespread species of the pine genus (*Pinus*), the Pine family (*Pinaceae*). It grows naturally in Europe and Asia. The tree is 25-40 m high. The trunk diameter is 0.5-1.2 m. The trunk is straight. The crown is highly raised, conical, further rounded, and wide, with horizontal branches arranged in whorls. The bark in the lower part of the trunk is thick, scaly, gray-brown, with deep cracks. The bark scales form irregularly shaped plates. In the upper part of the trunk and on the branches, the bark is thin, flaky (peeling), and orange-red. The branching is unimodal. The shoots are initially green, then by the end of the first summer, they turn gray-light brown. The buds are ovoid-conical, orange-brown, covered with white resin, more often with a thin, and less often with a thicker layer. The needles are arranged in fascicles by two, are 4-6 cm long, 1.5-2 mm thick, gray- or bluish-green, usually slightly curved, and the edges are toothletted. The upper side of the needles is convex. The lower one is grooved dense, with well-marked bluish-white stomatal lines. Male cones are 8-12 mm, yellow or pink. Female cones are 3-6 cm long, cone-shaped, symmetrical or almost symmetrical, single or grouped by 2-3, matte from gray-light brown to gray-green when ripe; ripen in November - December, 20 months after pollination; open from February to April and soon fall off. The scales of the cones are almost rhombic, flat, or slightly convex with a small navel, rarely hooked, with a pointed tip. The seeds are black, 4-5 mm in size, with a 12-20 mm membranous wing [117, 118].

Scots pine cone biomass was used to remove heavy metal ions from aqueous media. In particular, there are several articles on Cr(VI) ion adsorption from aqueous media by crushed *Pinus sylvestris* cones. Biosorption equilibrium, kinetics, and thermodynamics of Cr(VI) ions onto cone biomass were studied in a batch system with respect to temperature and initial metal ion concentration. The cone biomass of *Pinus sylvestris* exhibited the highest Cr(VI) uptake capacity at 45°C. The biosorption efficiency increased from 67% to 84% with an increase in temperature from 25 to 45°C at an initial Cr(VI) ions concentration of 300 mg/dm^3. The Langmuir isotherm model was applied to experimental equilibrium data of Cr(VI) ions biosorption depending on temperature. According to Langmuir isotherm, the monolayer saturation capacity (Qmax) is 238.10 mg/g. The pseudo-second-order kinetic model provided the best correlation of the used experimental data. The activation energy of biosorption (Ea) was determined as 41.74 kJ/mol [119]. It was determined that the greatest absorption of Cr(VI) ions was provided at pH = 1.0 [120].

Pine cones treated with 1M and 2M HCl solutions were used to remove Cr(III) and Cr(VI) ions at an initial concentration of the latter 100 mg/dm^3, pH = 1.0, and a contact time of 24 hours. It was determined that the sorption capacity for Cr(III) ions was 4.43 mg/g and for Cr(VI) ions – 4.60 mg/g [121]. Similar information was found in the dissertation [122] when *Pinus sylvestris* cones were treated with 0.1-2 M HCl solutions with a sorbate contact time of up to 24 hours at 20-40°C.

Two adsorbents were prepared from *Pinus sylvestris* cone and tinder fungus *Fomitopsis pinicola* biomass. It was found that adsorbents chemically modified with an HCl (activation 2mol/dm^3, activated for 60 min) demonstrated better Cr(VI) ions removal capabilities as compared to pure adsorbents in terms of their adsorption rate. The optimum conditions for removal of Cr(VI) ions were found to be particular size <0,5 mm, pH=1, contact time 10 min, adsorbent dosage 20 g/dm^3, concentration of Cr(VI) ions 100 mg/dm^3, temperature 25 ± 1°C. The percent removal at these optimum conditions was found to be 100 % for both biosorbents. The Langmuir model fitted the equilibrium data better than the Freundlich isotherm. The maximum uptake capacities are 40.98 mg/g and 45.05 mg/g for cone biomass and *Fomitopsis pinicola*, respectively [123, 124].

Response surface methodology was applied to optimize the removal efficiency of Ni^{2+} ions. *Pinus sylvestris* ovulate cones were used in this study. A 23 full-factorial central composite design was employed for experimental design and analysis of the results. The initial Ni^{2+} ions concentration - 10–30 mg/dm^3, pH = 2.5–6.5, and biomass concentration (5–25 g/dm^3) were the critical components of the removal optimized. The optimum pH, biomass concentration, and initial Ni^{2+} ions concentration were found to be 6.17, 18.8 g/dm^3, and 11.175 mg/dm^3, respectively. Under these conditions, the removal efficiency of Ni^{2+} ions was 99.91% [125].

Biosorption of Pb^{2+} ions onto cone biomass of *Pinus sylvestris* was studied with variations in the parameters of pH, initial metal ion concentration, and impeller speeds. Pb^{2+} ions removal rate was increased at pH = 4.0 and was sharply decreased when the pH of the solution was decreased to pH = 2.0. Impeller speed studies indicated maximum lead biosorption at 150 rpm, and the biosorption equilibrium was established after about 1 h. It was found that at an initial Pb^{2+} ion concentration of 100 mg/dm^3 and cone biomass content of 4 g/dm^3, the sorption capacity was 11.38 mg/g [126].

A study was conducted to assess the potential of Scots pine (*Pinus sylvestris* L.) cones for removing Cu^{2+} and Zn^{2+} ions from simulated solutions. It was found that pine cones have good adsorption properties for Cu^{2+} and Zn^{2+} ions from aqueous solutions with metal ion content of 1 mg/dm^3, a biosorbent concentration of 10 g/dm^3, and a contact time of 60 minutes. It was found that under these conditions, the removal rate reached 95% for Zn^{2+} ions and 96% for Cu^{2+} ions. It was also found that cone treatment with NaOH solution increases sorption characteristics. This provided a six-fold increase in the efficiency of sorbents with 5-2.5 mm and 2.5-1 mm fractions and a 30-fold increase in sorbents with a fraction of <1 mm [127].

The biosorption properties of Cu^{2+} and Zn^{2+} onto cone biomass of *Pinus sylvestris* L. were investigated by using batch techniques. The biosorption studies were carried out with single metal solutions. The removal of Cu^{2+} and Zn^{2+} ions from the aqueous solution increased with pH and sharply decreased when the pH of the solution was decreased. The maximum biosorption efficiency of Pinus sylvestris cones was 67% and 30% for Cu^{2+} and Zn^{2+} ions, respectively, at an initial metal ion concentration of 60 mg/dm^3 and a sorbent content of 2 g/dm^3. The Freundlich and Langmuir model can describe the adsorption equilibrium of metal ions on cone biomass. The second-order kinetic model was used to correlate the experimental data [128].

In addition to metal ions, Scots pine cone biomass was used to remove various dyes from aqueous media. In particular, the use of pine cone powder as an adsorbent for removing Methylene blue dye from aqueous solution was investigated. Within this scope, adsorption experiments were performed, and the results showed that the Freundlich isotherm model was a more convenient option than the Langmuir and Temkin models. Initial dye concentration was found to shift from 100 to 300 mg/dm^3, while adsorption capacity onto the pine cone powder changed from 40.99 to 95.24 mg/g, 41.56 to 97.93 mg/g, and 43.51 to 101.41 mg/g for 298K, 308K, and 318K, respectively. The results also determined that the pseudo-second-order kinetic model demonstrated higher correlation coefficients. The thermodynamic parameters for the instant free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) of this separation process were found by referring to -1595,11 J/mol, 2465,83 J/mol, and 12,77J/mol·K, respectively. The negative $\Delta G°$ values revealed that this separation process was endothermic and natural [129].

Also investigated the biosorption of Reactive Red 195 (RR 195), an azo dye, from aqueous solution by using cone biomass of *Pinus sylvestris* L. Maximum pH for efficient RR 195 biosorption was found to be pH = 1.0, and the initial RR 195 concentration increased with decreasing percentage removal. Biosorption capacity increased from 6.69 mg/g at 20°C to 7.38 mg/g at 50°C for 200 mg/dm^3 dye concentration. It is determined that the adsorption isotherms are more accurately described by the Langmuir model [57]. The pseudo-second-order kinetic model provided a better correlation for the experimental data. The activation energy of biosorption (E_a) was found to be 8.904 kJ/mol using the Arrhenius equation. The thermodynamic process parameters ($\Delta G°$= -13.25 - -17.56 kJ/mol at 20-50°C, $\Delta H°$= 29.42 kJ/mol, and $\Delta S°$= 144.67 J/mol·K) indicate physical endothermic adsorption [130].

Pine cone performance was also investigated for Basic Red 46 (BR 46) dye adsorption from aqueous solutions. Seventeen equilibrium isotherm models and eight kinetic models were compared at 298 K, 308 K, and 318 K for five different concentrations ranging from 20 to 60 mg/dm^3. The obtained adsorption data best-fit the Freundlich model among all the applied isotherm models, and the maximum adsorption capacity was calculated as 129.87 mg/g at 298 K. The pseudo-second-order model was the best choice to describe the adsorption behavior among all the applied kinetic models. The removal percentage of BR 46 dye with pine cones was 74.52% at 318 K for 60 mg/dm^3 concentration. The ΔG°, ΔH°, and ΔS° values of adsorption were calculated as −2.837 kJ/mol, 18.898 kJ/mol and 68.51 J/mol·K, respectively. This adsorption process was spontaneous and favorable, coinciding with the negative free energy. The activation energy (E_a) value of this process was determined with the Arrhenius equation as 19.92 kJ/mol [131].

2.12. The use of slash pine (Pinus elliottii) cones with other sorption materials.

Elliot pine or slash pine (*Pinus elliottii*) is a woody plant, a species of the Pine genus, the Pine family. It is widespread in the southeastern states of the U.S. The tree is up to 30.5 m tall. The trunk is up to 0.6 m in diameter, straight or curved. The crown is conical, spherical, or even. The bark is orange- or purple-brown, with intersecting grooves forming irregularly shaped scaly plates. The branches are spreading or upward; they are strong, up to 1 cm thick, orange-brown, darken and roughen with age. The buds are cylindrical, silvery-brown, 1.5-2 cm long; the scale edges are fimbriate. The leaves (needles) are arranged by 2-3 in a fascicle, diverge to the sides or upwards, remain on the tree for about 2 years, are 15-20 cm long and 1.2-1.5 mm thick, straight or slightly sinuous, flexible, yellow- or blue-green. The needles' edges are toothletted; the tip is sharply pointed. The male cones are cylindrical, 30-40 mm long, purplish. Female cones are symmetrical, arranged on a branch by one or in pairs, ripen every 2 years, fall off a year after dropping the seed, are narrowly ovate before opening and ovate after it, are 9-18 cm long, light brown, grow on petioles up to 3 cm long [132].

Several articles have been found on the adsorption of Cr(III) and Cr(VI) ions by *Pinus elliottii* cone biomass mixed with other sorbents. Thus, araucaria and pine cones, eucalyptus bark, and their aquatic extracts to evaluate their performance in the reduction/removal biosorption of chromium. The extracts obtained in the washing cycles at different pHs presented high organic loads. The pine is distinguished as the best biosorbent, and its performance is increased by prior washing in a natural medium. Eucalyptus extract produces the fastest reduction of Cr(VI) ions due to the presence of a high concentration of dissolved organic matter. The reduction of Cr(VI) ions to Cr(III) biosorption is a very quick reaction under tested conditions at pH = 2 in the presence of both washed and unwashed biosorbents, with the exception of basic medium washing. The extracts can be used in the treatment as the initial step process in reducing the Cr(VI) ions to Cr(III) ions. The washed biosorbents can be used to remove Cr(III) in combination with ensuring availability [133-135].

2.13. The use of unknown pine species cones removes various contaminants from aquatic environments.

Several articles have been found where the type of pine that gives the cones to be used as sorption materials to remove various pollutants from water is not specified. Thus, Almendros Molina *et al*. [136] model and optimize the elimination of Ni^{2+} ions from aquatic solutions by pine cone shells and olive tree pruning as biosorbents. A 33-full factorial design was employed for experimental design and analysis of the results. The flow rate (4-8 mL/min), the mass of biosorbent (5-15 g), and the initial Ni^{2+} ions concentration (10-100 ppm) were the critical variables of the removal optimized. The optimum flow rate, biosorbent mass, and initial concentration of Ni^{2+} ions to obtain the maximum total nickel ions removal coincided with both biosorbents and were found to be 6 sm^3/min, 15 g, and 10 ppm. Meanwhile, to maximize the biosorption capacity, the optimum flow rate, biosorbent mass, and initial concentration of Ni^{2+} ions were 6 sm^3/min, 15 g, and 100 ppm for the pine cone shell. The experimental breakthrough curves obtained under optimum conditions were modeled using Bohart–Adams, Thomas, Yoon–Nelson, and Dose-Response models. The last is the model that best reproduces the total breakthrough curves [136].

Several sorption materials, including crushed pine cones, were used to remove heavy metal ions (As(III), Cu^{2+}, Zn^{2+}, Mn(IV), Pb^{2+}, and Cr(VI)) from simulated solutions with varying pH values (2.5, 7.5 and 8.5). Initial metal concentration - Cu, Zn, Mn, Pb, Cr (10 mg/dm^3) and for As (1000 μg/dm^3); adsorbent dose - 0.5 g. Pine cones showed the same trend for metal removal efficiency - 99%, 97%, 96%, 88%, and 86% for Cu^{2+}, Zn^{2+}, Mn(IV), Pb^{2+}, and Cr(VI), respectively. Arsenic removal by pine cone biomass at pH 7.5 and at 3 h contact time was found to be 25% [137].

The pine cone was activated using NaOH solution and used in the adsorption of Malachite green dye. The compatibility of the experimental data with Langmuir, Freundlich, and Temkin isotherms was tested, and the results revealed that the data fits well with Langmuir type 2. Adsorption capacity is 111.1 mg/g and high adsorption value. The pseudo-second-order kinetic model was found to fit very well. The adsorption process was found to be an endothermic, spontaneous, and physical process according to thermodynamic parameters [138].

In addition, the adsorptive removal of 2,4,6-trichlorophenol using pine cone powder was discussed. The biosorption kinetic process was fast, reaching equilibrium in 75 min. On the other hand, the Langmuir isotherm model best described the equilibrium data with the maximum biosorption capacity (Q_e) of 243.90 mg/g. The experimental kinetic data showed excellent agreement with the pseudo-second-order model [139].

Biosorbent from pine cone powder was also used to treat wastewater contaminated with phenol and chlorophenols. Kinetic and equilibrium biosorption experiments showed that the uptake was more than 80% within the first 30 min of contact time at pH = 5.0. The biosorption of 4-chlorophenol onto pine cone powder was higher than those of phenol and 2-chlorophenol. The kinetic data were consistent with the pseudo-first-order kinetic model, and the Langmuir isotherm model best represented the equilibrium data. The maximum biosorption capacities of phenol, 2-chlorophenol, and 4-chlorophenol were 164.51, 189.44, and 220.12 mg/g at 30°C [140].

3. Conclusions

We have analyzed the literature data on the use of *Pinus trees (brutia*, *elliottii*, *halepensis*, *kesiya*, *koraiénsis*, *nigra*, *patula*, *pinea*, *radiate*, *resinosa*, *roxburghii*, *sylvestris*) cone biomass as sorption materials to remove metal ions, various dyes, and some organic compounds from simulated and industrial wastewater. This paper also provides brief information on the morphology of these *Pinus* trees. The work has proved that the sorption capacity of various species of pine cones for metal ions and organic pollutants can be improved by treatment with various chemicals. It was found that in most cases, the adsorption isotherms are more accurately described by the Langmuir model, and the kinetics of the process most often correspond to the pseudo-second-order model. It was found that, in most cases, the adsorption process has a physical nature.

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Conflicts of Interest

The authors declare no conflict of interest.

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