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Bioadsorbents for the removal of salt ions from saline water: a comprehensive review

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Abstract

Water quality can be affected due to organic or inorganic salts present in water depending upon different regions. An increase in salts has deteriorated the quality of the water, harming both human health and aquatic life. Various technologies are developed to extract salts, bioadsorption being the most preferred, eco-friendly, and economical method for desalination. To remove salts from aqueous solutions, an array of adsorbents, including natural, low-cost materials, or wastes, called bio-adsorbents are studied. The review aims at studying different bioadsorbents used for reducing salinity and the effect of pH, contact time, bioadsorbent dosage, initial concentration, temperature, and size of particulate matter on the removal efficacy of salts from saline water. The pseudo-second-order kinetics and Freundlich isotherm are the governing models that described salinity ions equilibrium and isotherm data. Prospects of the study including the potential for commercialization, scaling up, extensive applications of adsorbents, and their functional utility are discussed.

Keywords: Bioadsorbents, Bioadsorption, Desalination, Salinity, Water quality

Introduction

The management, use, and treatment of freshwater are facing a crisis due to its ever-increasing demand [1]. To supply freshwater that is suitable for agricultural use or suitable for human consumption in general, various nations around the world are investigating unconventional treatment technologies to remove salts and minerals from brackish or saline water [2]. Saline wastewater and effluents released unchecked and untreated may also pose a significant peril to humans and aquatic life [3].

Desalination is acknowledged as an option for meeting the longstanding requirements for drinking, industrial, and agricultural waters [4]. There are two main groupings of commercial desalination technologies such as membrane-based technologies like reverse osmosis (RO) and thermal-based technologies like multi-effect distillation (MED) and multi-stage flash (MSF). In addition, ion exchange, vapor compression, electro-dialysis (ED), capacitive deionization (CDI), humidification dehumidification (HDH), etc. are to a lesser extent common commercial technologies that endure shortcomings like excessive system costs, waste co-production, minimal efficiency, and inadequate performance [4, 5]. And the significance of desalination in removing the most significant impurities

from raw water, researchers have attempted multiple times to develop supplementary processes that can enhance desalination performance. In the desalination process, salt removal and water softening are viable steps.

Adsorption is a promising technology for the dissociation and exclusion of salts and several other ions from water due to its minimal development costs, flexibility, and ease of process design, operation, and upkeep [5, 6]. The variety and nature of the materials used as adsorbents have a significant impact on adsorption technologies and processes [7]. Desalination, water softening in terms of hardness removal, and salt removal have all been attempted using a variety of adsorbent materials [7]. Owing to the nature of the water, such as whether it is brackish or saline, the capacity of the treatment plant, and other factors, desalination is regarded as an expensive process [2]. Notwithstanding, treatment advances like utilizing bioadsorbents for desalination can successfully be utilized to eliminate salt from saline water because it requires insignificant costs and energy utilization is also less [8, 9].

Biosorbents are organic materials used for the elimination of contaminants from various natural and consumable resources. Biomaterials like algae, food waste, agricultural waste, bacterial, and industrial waste, and plant-based materials in their raw and natural form or modified form are among them. Since these come from renewable sources, are relatively inexpensive, easily biodegradable, and do not leave behind residual contaminants after use, they have received encouraging attention [10].

According to the literature review, numerous authors examined the use of different feedstock-derived bioadsorbents like banana peels, eggshells, tree barks, coffee husks, vegetable and fruit peels, and coconut squanders to remove various contaminants from water media under various operating conditions [11–16]. Contrary to live microorganisms, non-living biomass has an essential benefit in removing ions since it may be used for an extended period of time without nutritional input [17]. Therefore, [18] states that, plant-based biomass has been perceived as an assuring bioadsorbent for the abstraction of impurities from the water media.

Hemicellulose, starch, sugar in simplified form, lignin, proteins, lipids, water, and hydrocarbons are all common structural components of biological and agricultural wastes, each with distinct functional groups. Compared to the rest of the material, agricultural materials containing cellulose have a greater capacity for adsorption, such biomasses are often referred to as lignocellulosic material. As a cost effective adsorbent, various agricultural wastes have been documented, comprising of the shells or possibly stones of natural products like apricot stones, nuts, almonds, peanuts, cherries, and olive squander. This classification additionally incorporates squanders from the development of rice, corn, wheat, maize, sugarcane bagasse, and coir substance [9, 19]. In order to effectively adsorb cations, such as heavy metals and salts, lignocellulosic biomass has a strong potential to adhere to them [20].

As bioadsorbent materials suitable for remediating contaminants from effluents, various grains, organic products, seeds, vegetables, herbage, and forage, which address the most abundant waste in food and horticultural businesses, have extraordinary potential. However, for the best extraction and removal of impurities, the chemical and physical attributes of the bioresidues, as well as their activity boundaries (pH, contact time, bioadsorbent dose, temperature, initial concentration, particulate size of adsorbents,

adsorption energy, and isothermal behavior), should be taken into consideration in addition to the production volume [7].

The objective of this study is to assess the published data using a variety of bioadsorbents derived from agricultural waste and biomass of plant origin that have been used to remove salt ions from water media. This paper moreover centers around auditing the reasonableness of plant-determined biomass and waste-derived bioadsorbents, bioadsorption isotherm modeling, aspects influencing the cycle of bioadsorption, salt removal capability of various bioadsorbents in different experimental conditions, and so on, and alongside possibilities for future examination on salt ion biosorption are portrayed.

The mechanism involved in bioadsorption

“Adsorption is a phase transfer that takes place at solid–liquid or solid–gas interfaces” [21]. The inclination of chemical species in a medium to stick onto a solid is another way to describe it. Adsorption is the process by which molecules from whichever one, gas or liquid phase, accumulate close to a solid surface and become constrained to it through physical or chemical interlinkage. The adsorbent is the solid surface that provides the adsorption sites, and adsorbate is the constituent that is adsorbed on the solid’s superficial surface. By altering properties like concentration, temperature, pH, etc., an adsorbate can be liberated from a solid and returned to the primary phase. Desorption is the name given to this process [8, 22].

An adsorbate and adsorbent have extremely specific properties that are governed by their constituent elements. The process is referred to as physisorption if the collaboration between the molecules absorbed and the solid surface has a physical nature. The process results are reversible because the interactions in this instance are weak Van der Waals forces. In addition, it occurs near or below the adsorbed substance’s critical temperature. Conversely, if the forces of attraction among the solid surface and adsorbed molecules are induced by chemical bonding, it is referred to as chemisorption [23].

The principles for a good adsorbent as listed by [24] and [8] are—the adsorption capability of the adsorbent, shape, size, and chemical nature of adsorbent, good stability and durability of the adsorbent, particulate size, type of binder type, and the adsorbent’s micro-, meso-, and macroporosity, all contributing to the adsorption kinetics.

The improvement of bioadsorption processes for concentration, exclusion, and reclamation or recovering pollutants or contaminants from fluids requires a comprehension of the systems by which bioadsorbents eliminate such pollutants [25]. The rate, sum, and explicitness of contamination adsorption can be controlled through details of process limit and chemical or physical reactions that occur during bioadsorption are known [26]. The binding of sorbate to the bioadsorbent is an intricate process of biosorption mechanism. A biological matrix acts as the sorbent in biosorption, a sub-field of adsorption [27].

The principal frameworks responsible for known metal ions and cationic/anionic dye adsorption on bioadsorbents cellulosic in nature are chelating, reduction, ion exchanging, and assembly of structure with utile functional groups, precipitation, and liberation of the H_3O^+ group into a liquid solution [28–30]. During the phenomenon of ion exchange, the cell wall consists of positively and negatively charged ions associated with each other via the electrostatic force of attraction.

Bioadsorbents contain various functional groups like hydroxyl, ethers, carboxylic, amide, thiols, esters, carbonyl, phosphodiester, and imidazole. whereas some chemical groups like amine, nitrile, sulphonate, sulfate, and phosphates that can draw in and assemble metal ions [31]. Various investigations showed that the bioadsorption cycle can be integrated with ion exchange as opposed to complexation with utile/functional groups on the exterior of the biosorbent. They also demonstrated the roles that the adsorbent's sodium, potassium, calcium, and magnesium ions play during ion exchange [32–34].

Analysis of parameters affecting bioadsorption for desalination

Various parameters impacting the bioadsorption process are pH, contact time, temperature, the preliminary concentration of the solute, bioadsorbent dose, agitation speed, and particle size are discussed in the following section.

Effect of pH variation

The mechanism of adsorption is revealed by the pH of the solution [35]. pH affects the adsorption capacity because it significantly impacts the exterior charge of the adsorbent and the formation of new species of the adsorbate [18]. At various pH levels, the functional group ionic charge and metal speciation have a significant impact on the bioadsorption performance. Positively charged cations are drawn in by negatively charged biomass at low pH values (in acidic conditions). Cations interact with OH^- ions particles, depending on the solubility product constant (K_{sp}) values of metal hydroxides, and precipitate at higher pH values. The solution's concentration of hydroxyl ions rises in tandem with an increase in pH. Metal ions precipitate at alkaline pH levels, making the bioadsorption process nearly impossible. It is necessary to investigate the solute's pH upper limit [36, 37].

Kumar and Singh [35], Shanmugasundaram and Sudalaimani [38] studied the optimum pH specifications for the exclusion of chloride ions from water using bioadsorbents Parthenium (congress grass) and *E-crassipes*, respectively. The experimentations were conducted for pH variations ranging from 2 to 14. The optimum pH was obtained between 6 and 7, for which the highest removal efficiency was achieved. As the pH was raised, the removal efficiency improved. Until it reached optimum pH post which the removal efficiency decreased. Similarly, [39] studied the optimum range for maximum sodium ions removal. Even though a neutral pH had a significant capacity for sodium removal, the optimal pH was obtained to be 2.

The point of zero charge (PZC), as expressed by [40], is the pH value that corresponds to the equilibrium point of the external as well as internal charges of the adsorbent material. Amaringo and Anaguano [41] says that pH values of solution above PZC of the adsorbent implies the exterior of the adsorbent is negatively charged, whereas pH values of solution below PZC of the adsorbent means the surface is positively charged. Subsequently, [42] studied pineapple peel as a bioadsorbent for the amputation of copper ion from water. The pineapple peel had a PZC value of 5.0, indicating that pH values greater than the PZC are expected to produce an adsorbent with a negatively charged exterior surface and prefer the positively charged copper ions adsorption. In 60 min of contact

time interval, at pH=5, an elimination of 50% was achieved for concentrations ranging from 2 to 10 mg/L of the solute.

The optimum range for pH depends upon the bioadsorbent used and the removal of the intended ions. Rima et al. [43] analyzed the consequence of pH modification on adsorption capacity for a column packed with dry beetroot powdered fiber. With increasing pH, the percentages of fixed CaCl_2 and NaCl reached 98 and 96%, respectively, at pH 6.5. Also, [44] studied the removal of sodium ions using Beetroot pulp (BP) and Sugarcane bagasse (SCB). The optimum pH obtained was 10.0 and 6.0, respectively, for sodium ions with BP and SCB. Over a wide pH range, the different chemical compositions and, as a consequence, functional groups of various bioadsorbents result in varying efficiencies for metal ion removal and extraction [44]. Cations (positively charged ions) and H^+ ions contend for system exchange sites at lower pH values, partially releasing cations. The adsorbent surface tends to be more negatively charged at high pH values, raising the cationic attraction to the adsorbent up until it reaches its peak around optimal pH owing to the decline in Coulombic repulsion of metal ions [45].

Effect of bioadsorbent dose variation

The dosage of a biosorbent has a substantial impact on the bioadsorption process because it provides the sites for attachment for metal biosorption [30]. Owing to the enhanced surface area and consequently increased number of binding sites, an increase in the bioadsorbent dose at a given preliminary metal concentration increases the bioadsorption of metal ions [46]. The measure of metal biosorbed per unit weight of the biosorbent is large at lower dose of the bioadsorbent. On the contrary, the quantity of metal ion biosorbed per unit weight declines at higher dosages of the bioadsorbent. Since there is insufficient solute present for entirely spreading onto the potential and accessible binding sites, the adsorbate-to-binding site ratio is reduced [30, 47].

The bioadsorption of salinity ions by *Phyllanthus Emblica* and *Cynodon Dactylon* was enhanced as the biosorbent quantity rose from 0.2 to 1.0 g/200 ml of saline water. The optimum dosage for both the bioadsorbents was found to be 1 g/200 ml where maximum removal efficiency was achieved [48]. Ahmed [44] when investigating the consequence of dose variation for extraction of ions viz sodium and lead using sugarcane bagasse (SCB) and Beet pulp (BP), found that the percentage of extraction of sodium ions rose to 97.5% from earlier 18% as the quantity of bioadsorbent varied from 0.1 g/50 ml to 4 g/50 ml for SCB whereas the percentage of extraction rose to 98.9% from 35% as the dose varied from 0.1 g/50 ml to 2 g/50 ml. The increase in the dose increased the active binding site for the adsorbate on the surface of the bioadsorbent.

Kim et al. [39] studied raw used tea leaves of green tea (GT), peppermint (PM), and chamomile (CM) as bioadsorbents for the desalination of seawater. While PM did not alter the affinity for sodium, higher masses enhanced CM's adsorption. GT, on the other hand, was significantly affected as mass increased. Problems with aggregation under batch conditions may provide an explanation for this. Of the three bioadsorbents used in the study, GT had the highest mass and thus sank to the bottom of the tube thereby reducing the possibility of interaction between sodium ions and solid surface area. CM, alternatively, is a very light bioadsorbent that, even at high masses, can be easily

distributed in the solution. Based on these findings, the ideal dosages for CM, GT, and PM were attained as 150, 75, and 75 g/L, respectively.

In another study, [49] confirmed that the bioadsorbents in the range of 0.05% to 1% concentration would be ideal for salt reduction in irrigation water. Another finding suggested that bioadsorbents when used in powder form showed better performance in reducing the EC than in non-powder form.

Moringa oleifera's ability to remove hardness was observed to improve with dose, as investigated by [50]. The quantity of dose of bioadsorbent requirement to obtain equivalent residual hardness for water with an identical initial hardness depends upon the quantity of hardness causing ions present in the water sample. The study identified a threshold *Moringa oleifera* dose concentration of 650–750 mg/L for synthetic hardwater.

Effect of contact time

The type of bioadsorbent, ion concentration, and its amalgamation determine the total time entailed to reach maximum biosorption [30]. At the beginning of the experiment, abundant active sites are present which are responsible for the initial speedy bioadsorption of ions. Over time, the rate of biosorption decreases since the residual ion percentage in the solution decreases [19].

Kumar and Singh [35] studied the removal of chloride ions using *Parthenium* grass with a constant pH of 7, the bioadsorbent dose was kept to 1 g/L in a rotating system of 500 rpm, with variation in the contact period from 10 to 240 min. It was examined that the percent of bioadsorption raised with an increment in time of contact [35].

With the increment in contact time for adsorption (30 to 210 min), the removal rate increased from 34 to 91% for sodium ions. In a similar vein, 91 mg/g adsorption capacity was achieved at the contact time succeeding 210 min. No notable rise in removal of sodium ions was reported after varying contact time from 150 to 210 min. Due to active sites initially available on the exterior of the adsorbent, the removal efficacy was higher at the commencement of the experiment. However, as the available active sites engage with the ions, it gradually reduces the removal rate of adsorption after achieving equilibrium [51].

In another study carried out where Neem and Kikar leaves were used as a mixture in different proportions to extract fluoride from water [52], the maximum extraction was obtained for the ratio 2:1 (Neem: Kikar). The fluoride removal increased from 44 to 63.6% as the period of contact was raised from 15 to 120 min. The higher initial removal may be attributed to electrostatic affinity, empty adsorption sites, ion exchange, and high solute concentration gradient [53].

Many researchers have stated that the primary step in the adsorption mechanism occurs due to ion sorption onto the surface whereas the next step occurs due to intraparticle transference from bulk solute to the adsorbent's porous exterior surface. The process of adsorption in the earlier stages of the experiment is rapid since the accessibility of unoccupied regions on the surface of the adsorbent are more providing ease of admission for ions. With the passage of time, the sites become unavailable since the surface becomes saturated with ions. Thus, it can be stated that the time for adsorption is rapid in the beginning, however, it slows down towards the equilibrium [54, 55].

Nevertheless, repulsive interactions between molecules present in the solute in the solid and bulk phases make it complicated to fulfill the remaining empty spaces [51].

This was also highlighted by [56] stating, the solution's high adsorbate concentration may function as an impetus to transfer further adsorbate to the adsorbent surface. However, since no more adsorbates can be added to the adsorbent's surface after it has been covered in adsorbate, the adsorption capability decreases, and the percentage of adsorbate removed correspondingly decreases.

Effect of initial concentration

The preliminary concentration of metal ions can be leveraged to prevail over the mass transfer barrier intervening the fluid and solid phases [57]. The amount of bioadsorbed metal ions per unit weight of the biosorbent is commonly referred to as the bioadsorption capacity, and it initially improves along with the rise in metal ion concentration until reaching a saturation value. Although, when the concentration of metal ions rises, the biosorbent's biosorption effectiveness declines. The entire interaction of ions with the accessible binding sites leads to greater rates of efficacy, which accounts for the elevated bioadsorption efficiencies at low metal concentrations. The saturation of accessible binding sites causes a high proportion of metal ions to remain liberated in the solution at greater concentrations [58].

For instance, both Na⁺ and Mg⁺ cations, the equilibrium adsorption capability rises with the preliminary concentration of solutes containing salt as stated by [19]. The concentration gradient that exists concerning adsorbate and the original amount of cations affects the elimination of cations by adsorption. As a result, this adsorption–desorption equilibrium condition is achieved more quickly and results in reduced adsorption capacity at low cation concentrations in the medium. Particularly if the adsorption is a single-layer coverage, the relationship is more obvious.

A reasonably price-effective bioadsorbent was produced by carbonizing *Phragmites australis* reed at 500 °C, as studied by [51]. Differing on the initially set concentration of the respective batch, the results discovered when the preliminary concentration varied in the range 20 and 100 mg/L confirmed that both the removal efficacy along with the adsorption capability increase when the preliminary concentration is raised within or below the thresholds of adsorption capacity. NaCl removal ranged from 50 to 92% as the removal percentage increased linearly. With a fixed amount of bioadsorbent, a higher initial sodium (Na⁺) concentration resulted in a higher sodium (Na⁺) concentration in the solution and more sodium being absorbed by the adsorbent. A significant mass transfer driving force is the cause of an upsurge in adsorption with an upsurge in sodium [59].

Effect of particle size

Caesalpinia bonducella leaf powder's particle sizes (50, 75, 100, and 125 μm) affected copper (II) adsorption. The removal efficiency decreased due to a decrease in the binding rate and surface area of the functional groups accountable for bio-adsorption and metal ions, with an increase in the particle size of bioadsorbent. The efficiency of adsorption decreases from 85.22 to 72.46 and further declines to 32.23% as the particle size increases from 75 to 100 and then 125 μm [60].

In most of the pertinent literature referred to, it was observed that the size of the bioadsorbent particle ranged from 0.5 to 0.85 mm and the removal efficiency ranged between 38 and 98% [7, 35, 44, 61]. Maximum removal was obtained of 52.85% with a particle size of 2 mm [62]. In the similar range wherein the bioadsorbent particle size utilized was 2.26 mm the maximum removal obtained was 60% [53].

Effect of temperature

As per the thermodynamics of the biosorption cycle, temperature assumes a critical part in the sorption of ions and is straightforwardly connected with the dynamic energy of the particular ions present in the solute. As a result, it may symbolize the diffusion procedure. The amount of metal absorbed by the biomass should shift in response to changes in temperature [63].

Important process parameters include Gibbs free energy (ΔG), change in enthalpy (ΔH), and change in entropy (ΔS). The spontaneity of the adsorption cycle can be seen in negative ΔG [64]. Using ΔH , it is possible to determine the nature of adsorption. A response that has a positive worth of ΔH indicates that it is endothermic, while a response that has a negative worth of ΔH signifies that it is exothermic [64, 65]. Adsorbate molecules are more randomly distributed on the exterior of solids than in solution if the ΔS value is positive [66].

Alagumuthu et al. [31] monitored standard changes in free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) were calculated and presented under optimized conditions and thermodynamic parameters, indicating the endothermic nature of the diffusion-controlled adsorption process. *Cynodon dactylon*'s sorption was monitored at 303, 313, and 333 K at four distinct temperatures. Negative ΔG values demonstrated the spontaneity of the sorption reaction. Positive ΔH values denoted the endothermic nature of the bioadsorption process. The findings demonstrated that fluoride's adsorption capacity increased with temperature. This recommends that the diffusion peculiarity controls the adsorption interaction. The results confirm that the diffusion-controlled adsorption process is endothermic as a result. Similar results were also noted by [67] for zirconium-modified Cashew nut shells for four distinctive temperatures 303, 313, 323, and 333 K under the optimized condition. The improvement of adsorption at higher temperatures might be credited to the augmentation of pore size or potential activation of the bioadsorbent surface [68].

Rolence et al. [53] explored the effect of temperature (303, 313, 323, and 333 K) variation on adsorption and consequently witnessed that the adsorption improved with a rise in temperature. A conceivable justification behind the observation is expansion of the bioadsorbent due to temperature, which allows more dynamic active sites accessible for hardness causing ions to permit adsorption. Furthermore, the study demonstrated that Coconut Shell Activated Carbon's adsorption of hardness ions is endothermic in nature owing to the fact that adsorption increases with temperature.

Subsequently, in order to verify the adsorption isotherms and the essential parameters for setting up large-scale pilot plants, the adsorption studies were conducted at 25, 35, and 45 °C by [69]. The endothermic attribute of the process was demonstrated by an increase in fluoride uptake with temperature. On H-type carbon, activated at 600 °C,

the fluoride uptake was noticed to be higher (72–98%) than on L-type carbon (51–93%), activated at 200–400 °C.

Nature of bioadsorbents

As per [70], a good adsorbent should have an enormous surface area, a high adsorption limit, large porosity, simple accessibility, simplicity of recovery, and high selectivity along with being eco-friendly in nature. High adsorption limit is a consequence of the adsorbent's larger surface region in conjugation with higher porosity, besides lower ash content. Important variables that are determined on the surface of biomass-based adsorbents include the adsorptive process and the hydrophobic nature or hydrophilic characteristics of bioadsorbents [71]. A rise in Na⁺ sorption capability was noted by [72] as surface area increase. Ion migration across the bulk solution towards the exterior of the adsorbent is accelerated by high surface area. The ability of molecules to penetrate to the interior of the adsorbent determines the capacity for sorption of carbon porous materials. The interior surface of the adsorbent materials is easier to access due to the pores' bigger diameter than the size of the adsorbate.

In order to comprehend the impact of adsorption capabilities, [39] investigated the effect of altering the surface characteristics of tea leaves by pre-treating them with acid (HCL) and base (KOH). To boost the absorption of sodium ions, which was seen to rise by a factor of 2.5, the researcher claimed that active functional groups of the bioadsorbent needed to be activated by adding the acid and bases. Similarly, large porous structure was also reported by [53] during the activation process of the CSAC bioadsorbent.

Biosorbents made from plant biomass often have very uneven and irregular surfaces that are extremely heterogeneous and covered with spaces, voids, splits, gaps, fractures, nooks, fissures, and crevices. These traits serve as locations that boost the activity of surface sorption. The particle's surface area increases as it acquires surface heterogeneity, making it more effective for the sorption of contaminants [73]. Similar profiles with vessels, voids, and pockets as studied by [39] are seen in both GT and PM, which are advantageous morphological characteristics for a bioadsorbent. These cavities and crevices can act as intricate circuits for the movement of sodium ions, which are then conveniently captured by the inner bioadsorbent surfaces. As opposed to GT and PM, CM exhibits a more homogenous surface with openings and troughs. The comparatively lower adsorption of CM, when assessed along with both GT and PM, could potentially be attributed to the different textural and morphological characteristics of the adsorbent.

Marathe et al. [74] continued by stating that greater specific surface areas and greater water-holding capacities in rice straw, charcoal, coconut husk, and rice kernels enable a greater proportion of inorganic salts and other contaminants from the water and wastewater to be absorbed. As a consequence, the surface area and porous structure of the bioadsorbents as well as the chemical interventions involving the functional groups of bioadsorbents, and inorganic ions present in the water and wastewater influence the pollutants' ability to be absorbed.

The functional groups and the pore volumes of the bioadsorbent determine the rate of adsorption. The bioadsorbent can adsorb ions to its surface adhering to its larger pore volume structural property [75, 76]. The amount and availability of functional groups on the exterior of the bioadsorbent are key factors in the bioadsorption process; altering

these surface properties can have a significant impact on the capability of employing a bioadsorbent for eliminating ions [77]. In accordance with [53], among the functional groups discovered for the adsorption of hardness ions upon the CSAC bioadsorbent surface and resulting high efficacy in water softening were alkane, hydroxyl, amine, alkoxy, and nitro groups. Consequently, the findings, which [43] have already been published, demonstrate the existence of several different chemical groups on the beetroot fibers. The primary type of chemical and functional groups on the fibers are carboxyl and aldehyde, coupled with nitrile groups. These are well recognized for their ability to fix cations.

Different types of bioadsorbents utilized for desalination

In desalination applications, [19] investigated the capability of activated coconut coir (ACC), prepared in the laboratory, to remove Na^+ and Mg^{2+} ions from saline water. Dust from raw coconut coir was pyrolyzed with 50% H_3PO_4 acid to make activated coconut coir. The standard 0.2 mol/dm^3 NaCl and MgCl_2 ion removal efficiencies were observed to be approximately 50%. 80.0 g/L was found to be the optimal dosage of activated coconut coir (ACC) for removing 40% of both cations from seawater. Through repeated filtration, activated coconut coir can eliminate up to 72% of Mg^{2+} and 80% of Na^+ from seawater. The adsorption capability attained by Activated Coconut coir was 416.3 mg/g and 481.3 mg/g for Na^+ and Mg^{2+} ions, respectively. Using pyrolysis and back washing with distilled water, the used ACC was positively regenerated.

The sodium ions in seawater could be removed from seawater using spent tea leaves [39]. Although the findings demonstrate a robust effect of variation in pH, salt concentration, the quantity of bioadsorbent, the presence of additional ions, and dyes, the findings do not demonstrate a remarkable salt removal efficiency using the bioadsorbents (maximum observed adsorption percentage of 8%). Based on the fact that base-treated green tea leaves showed adsorption of 16%, this suggests that these materials have the potential to improve desalination. These materials have the right morphological and textural properties, as well as a high heat resistance, according to instrumental analyses, which suggests that they have the right mechanical properties to be used as adsorbents. Lastly, treating the tea leaves with dilute acids and bases improved their ability to absorb sodium ions, indicating their potential as biomaterials for desalination.

Aghakhani et al. [7] studied 21 batch experiments to check the potential of 05 adsorbents namely activated carbon, anionic resin, peat, cationic resin, and zeolite—to be used alone or in combination to eliminate from aqueous solutes consisting of salinity ions. The conclusions of this investigation showcased that activated carbon had the highest adsorption rate of 255.5 mg/g whereas lowest adsorption rate was observed for peat, i.e., 253.7 mg/g, in saline water with total dissolved solids, i.e., TDS of 13.32 g/L. The adsorption rates of salinity ions were identical in anionic resin, zeolite, and cationic resin. The study's main finding was that the combination of activated carbon, cationic resin, peat, anionic resin, and zeolite produced the greatest salinity reduction.

Investigative studies were conducted by [49] to select appropriate plant-origin bioadsorbents for lowering the EC of bore well water (EC 2.20 dS/m). Against salt reduction, 27 bioadsorbents were tested. The EC was effectively decreased from 1.89 to 1.63, 1.68, 1.69, 1.73, and 1.77 dS/m, respectively, by neem bark, calotropis flower, Prosopis leaves,

and amla stem. Reduction in EC was observed when bore well water was treated with neem bark powder at a concentration of 0.05% (0.39 dS/m in 168 h of time of contact). In an Azolla multiplication tank, the neem bark powder at a concentration of 0.05% was successfully used to reduce salt from 2.13 to 1.83 dS/m. Azolla did well in water with an EC of 1.83 dS/m, but it did not do well in water having EC of more than 2.0 dS/m.

Utilizing organic materials like, raw rice straw, raw coconut husk, raw rice husk and charcoal, [74] determined the plant-based treatment efficacy for treating moderately saline wastewater. With a rate of 200 m³/ha/day, saline wastewater of moderate strength with TDS concentration of 6143.33 ± 5.77 mg/L was employed to five distinct treatments in lysimeter (T1, T2, T3, T4, and T5). Charcoal, coconut husk, rice husk and rice straw were utilized as filter bedding materials (FBM) in the T5, T4, T3, and T2 treatment systems, respectively, while T1 served as a control system with no filter bedding material. T3 had the maximum removal efficacy with 76.21%, pursued by T4 (67.57%), T5 (65.18%), T2 (46.46%), and T1 (45.5%). Sodium (Na) and potassium (K) accumulation were also higher in T3 and T4. The most encouraging outcomes were gotten for T4 and T3 in correlation with the control (T1), which suggests that, among all-natural substances, rice and coconut husk demonstrated the most noteworthy ability for salt removal.

Bhatnagar and Sillanpää [9] analyzed the use of naturally available low-priced materials like coconut shell activated carbon, rice husk ash, wheat straw ash and Amorphophallus campanulatus (Elephant foot yam) for their effectiveness in the elimination of hardness-causing ions from water. The investigation was conducted to also understand the consequence of variation in optimizing parameters such as period of contact, the quantity of adsorbent, and pH on removal efficacy. It is apparent from the batch studies' experiments that activated carbon from coconut shells removes hardness (by more than 60%) while wheat husk ash has a lower removal rate (less than 30%) and Amorphophallus campanulatus can be utilized to eliminate hardness due to its rational efficacy (more than 80%). When the pH is around 8, the removal rate was found to be more.

Niranjan et al. [62] found that the best results were obtained when 400 mg/lit of Coconut Shell Activated Carbon (CSAC) was mixed and treated with 50 ml of water sample for one hour, resulting in a reduction of 52.85% in the hardness of the water sample. This was done with the aim of reducing the amount of chloride and hardness that were present in the water sample. Coconut shell activated carbon (CSAC) was studied at varying concentrations and intervals to reduce chloride. Chloride, on the other hand, had a maximum removal rate of approximately 24.24% after 75 min of contact with the same dosage.

Kharel et al. [78] measured the treated water samples' removal efficacy, water hardness and pH changes. As the dose of ash increased, so did the water's pH and effectiveness at removing hardness. Wheat straw ash (WSA) and rice husk ash (RHA) achieved maximum removal of 81% (at 17.5 g/l with an adsorption capacity of 67 mg/g) and 58% (at 22.5 g/l with an adsorption capacity of 44 mg/g) respectively. The higher concentrations of alkali metal oxides in WSA resulted in a higher hardness removal efficiency. The results imply that ashes obtained from locally available material may be useful in the process of removing hardness. Although the water being treated is softened, due to relatively higher concentrations of alkalinity, the softened water cannot serve as potable

water. This is in line with the fact that wheat straw ash also increased water samples' pH compared to RHA, which decreased removal efficiency.

Rolence et al. [53] used coconut shell activated carbon (CSAC) as a low priced naturally available bioadsorbent in batch tests to explore the effects of several bioadsorbent parameters such as the amount of bioadsorbent, period of contact, preliminary pH, and temperature on the mechanism of adsorption using synthetic and field-obtained water samples. Removal efficacy was 60% and 55% for both synthetic and field-collected water samples at a well-almost pH of 6.3. The percentage removal improves with increasing contact period and bioadsorbent dose until it reaches 15 h and 0.24 g/ml for both fields and chemically synthesized hard water, which is regarded as the maximum. The removal efficacy of synthetic water was discovered to be greater than that of field water. Because field water contains various ionic contaminants, its solution concentration is evidently high in comparison.

Other desalination applications of biomaterials are presented in Table 1:

Isotherm modeling involved in bioadsorption process

The equilibrium relationships concerning bioadsorbent and sorbate, the mass of the biosorbed component per unit mass of bioadsorbent, and the concentration of sorbate in the medium under a particular set of specifications (temperature and concentration) can all be explained using adsorption isotherms [80]. A curve that describes the retention of a substance on the exterior of solids at various concentrations can be termed "isotherm" [63]. The fundamental step in developing an effective biosorption system is determining the influential equilibrium parameters. Linear regression is often applied to find the sorption isotherm that fits the best. The least squares method is utilized to predict the isotherm parameters [30].

The Langmuir isotherms are centered on three hypotheses: (i) an adsorbate that is emphatically drawn to the outer layer of the adsorbent is available on the adsorbent's surface; (ii) the surface has a predetermined number of spots where the solute's molecules can be adsorbed; (iii) the adsorption incorporates the association of only one layer of particles to the surface, for instance, monolayer adsorption [81, 82]. Freundlich isotherm, existing as an empirical equation, often broadly involves isotherms for the clarification of adsorption equilibrium. The adsorption of heavy metals on an extensive range of biosorbents can be analyzed using the Freundlich isotherm [81, 82]

Both straightforward fundamental models (Langmuir and Freundlich models) likewise do not consolidate the impacts of any external variables, in spite of the fact that they are fit for portraying numerous bioadsorption isotherms as a rule. Biosorbents and their multiple active sites, and complex chemistry of some metallic compounds, can also cause biosorption isotherms to exhibit an irregular pattern [83].

For instance, the linear illustrations of the Langmuir model employed for the bioadsorption of Na^+ ions onto the biomasses of SCB and BP are presented in the work of [44]. The researchers specified that the value of correlation coefficient (R^2) was superior in the case of the Langmuir model than for the Freundlich model, implying that both SCB and BP biomass surfaces are made up of homogeneous adsorption patches, signifying the development of monolayer coverage of Na^+ ions on the outer surface of the biosorbent.

Table 1 Summary of bio-adsorbents used for removal of salinity-causing ions

Bio-adsorbent used	Mode of study	Variation in parameter	Conditions of equilibrium for maximum removal efficiency	Maximum removal efficiency (%)	Maximum adsorption capacity	Reference
<i>E. crassipes</i>	Batch	Dose: 1 to 6 g/50 ml Initial concentration: 100 to 200 mg/L of Cl ⁻ ions pH: 2 to 14 Contact time: 1 to 6 h	Dose = 4 g/50 ml Initial concentration = 150 mg/L pH = 6–7 Contact time = 4 h	45%	NA	[38]
Phyllanthus Emblica and Cynodan Dactylon	Batch	Dose: 0.2 to 1 g/200 ml Contact time: 15 to 240 min	For Phyllanthus Emblica: Contact time = 240 min Adsorbent dose = 1 g/200 ml Cynodan Dactylon: Contact time = 240 min Adsorbent Dose = 1 g/200 ml	For Phyllanthus Emblica: 56% Cynodan Dactylon: 44%	NA	[48]
Parthenium (congress grass)	Batch	pH: 3 to 11 Initial concentration: 100 to 1000 mg/L of Cl ⁻ ions Contact time: 10 to 240 min Dose: 1 to 7 g/L	Optimum pH = 7 Initial concentration = 100 mg/L Adsorbent dose = 1 g/L Contact time = 5 min	88%	24.39 mg/g	[35]
Umbu seed (<i>Spondias tuberosa</i> Arruda Câmara)	Batch	Initial Concentration: 100–300 mg/L of NaCl synthetic sample Real water sample EC concentration = 1321–2280 μ S/cm Contact time: 10, 20, 30 min, and 1, 2, 3 h Dose variation: up to 1 g/100 ml	Adsorbent dose = 1 g/100 mL Initial concentration: EC = 2280 μ S/cm Contact time = 10 min	39%	250 mg/g	[79]
Sugarcane Bagasse and Beet Pulp	Batch	pH: For Bagasse and Beet Pulp: pH = 2–10 For Bagasse: Dose = 0.1–4 g/50 mL for Beet Pulp: Dose = 0.1–2 g/50 mL Contact time = 10, 30, 45, 60, 90, and 120 min	For Bagasse: pH = 6, Adsorbent dose = 4 g/50 mL, CT = 120 min For Beet Pulp: pH = 10, Adsorbent dose = 2 g/50 mL, CT = 90 min	For Bagasse: 97.5% For Beet Pulp: 98.9%	NA	[44]
Phragmites australis reed	Batch and Continuous	pH = 2 to 10 Dose = 2 to 10 g/L Contact time = 30 to 210 min Agitation speed = 100, 150, 200, and 3000 rpm Initial concentration = 2000 to 10,000 mg/L of NaCl	Contact time = 150 min pH = 4 and Adsorbent dose = 10 g/L Agitation speed = 300 rpm	90%	117.68 mg/g	[51]

Table 1 (continued)

Bio-adsorbent used	Mode of study	Variation in parameter	Conditions of equilibrium for maximum removal efficiency	Maximum removal efficiency (%)	Maximum adsorption capacity	Reference
Cynodon dactylon based activated carbon	Batch	pH = 6–7 Initial Concentration = 2, 4, 6, 8, and 10 mg/L Temperature variation = 303, 313, 323, and 333 K Dose = 0.25 to 2.25 g/100 ml Particulate size = > 53, 53–106, 106–150, 150–225, and 225–303 μm Contact time = 15–195 min	Initial Concentration = 3 mg/L of F ⁻ ions Adsorbent dose = 1.25 g/100 ml pH = 6–7 Agitation speed = 250 rpm Particle size = 53 μm Contact time = 105 min	83.77%	4.702 mg/g	[31]

Numerous isotherm models can be found in the literature to refer to the probable mechanism of the sorption process and the equilibrium bioadsorption distribution. Table 2 summarizes the best-fitting isotherms of the Langmuir isotherm and the Freundlich model, two of the isotherm models most commonly used in salt ion bioadsorption research.

Kinetic modeling involved in the bioadsorption process

As the system’s kinetics verify the adsorbate residence period and reactor size, predicting the rate of adsorption for a given system is one of the most principal aspects of adsorption system model. Equilibrium studies are required to govern whether adsorption is effective. Additionally, it is critical to identify the type of adsorption component in a given framework [84]. Using kinetic models, mass transport along with processes involving chemical reactions, have been analyzed. Predicting the adsorption rate for a given structure is amongst the main components in the adsorption system plan [81].

Table 2 Best-fitting isotherm models applied in the bioadsorption of salinity-causing ions

Isotherm	Linear form	Bioadsorbent	Reference
Langmuir model	$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{k_l q_m}$	E. crassipes	[38]
		Parthenium grass	[35]
		SCB and BP	[44]
		Cynodon dactylon based activated carbon	[31]
Freundlich model	$\log q = \log k_f + \frac{1}{n} \log C_e$	Neem (Azadirachta indica) and Kikar (Acacia arabica) leaves	[52]
		Activated coconut coir	[19]
		Amorphophallus campanulatus (Elephant foot yam)	[61]
		Coconut Shell Activated carbon	[53]
		Phragmites australis (Reed)	[51]

With the intention of exploring the mechanism of bioadsorption, various researchers have studied the Kinetic Modelling for salt ion adsorption, and are characterized in Table 3:

Applicability of the bioadsorption processes

The sample obtained from an adjacent community with an elevated fluoride level allowed [31] to assess the defluoridation effectiveness of *Cynodon dactylon* at the actual level. A fluoride water sample of 100 mL, which was subsequently added with 1 g/100 ml of the adsorbent dose and agitated continuously for a set period of time at ambient temperature. In addition to the quantity of fluoride, other indicators of water quality have significantly decreased. The outcome clearly shows that the sorbent can be beneficially utilized in the actual field. About 67.19% of the fluoride was reduced, whereas 39.88% of the electrical conductivity was reduced from the measured value. Chloride content was successfully decreased by *Cynodon dactylon* to around 86.66%.

In another study, [44] at room temperature, soaked 4.0 g of SCB and 4.0 g of BP in the different NaCl concentrations (100, 200, and 300 mM) for an overnight period before being filtered. Zea maize and wheat plants are irrigated with the filtrate. By calculating the mass and leaf areas of the two plants it was possible to determine if their development has improved. According to prior batch study findings, SCB and BP bioadsorbents may be appropriate for the adsorption of sodium ions at optimal pH values of 6.0 and 10.0, respectively. However, the plants do not grow well at these pH levels. As a result, a balance between pH levels that allow for well expansion while also lowering sodium ion concentration in water is required. Using SCB and BP, the percent of Na(I) removal has been determined to be 60 and 88%, respectively. The figures are suitable for lowering sodium ion concentrations in water to enhance plant development [82].

In order to inspect the actual impact of the studied bioadsorbent on natural water samples, researcher [52] collected four natural water samples from Rohtak. The fluoride content in the water sample was analyzed to be 2.6 mg/L. An adsorbent dose of 2:1 of ANC: AKC could reduce the fluoride levels to 1 mg/L, which is within the acceptable range for drinking water [85].

Rolence et al. [53] used CSAC to conduct similar research to compare the adsorption trends of natural water and synthetic water. Although the adsorption trend showed a similar pattern, the removal effectiveness varied noticeably, according to the study.

Table 3 Best-fitting kinetic models applied in the bioadsorption of salinity causing ions

Kinetics	Linear form	Bioadsorbent	Reference
Pseudo-first order model	$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t$	SCB and BP	[44]
		<i>Cynodon dactylon</i> based activated carbon	[31]
Pseudo-second order model	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$	Neem (<i>Azadirachta indica</i>) and Kikar (<i>Acacia arabica</i>) leaves	[52]
		Rice Husk activated carbon	[72]
		Phragmites australis (Reed)	[51]

Where

- q_e and q_t (mg/g) are the sorption capacity at equilibrium and at time t (min), respectively and
- k_1 is the rate constant of the pseudo-first order equation (min^{-1})
- k_2 is the rate constant of pseudo-second order sorption (g/mg min)

It was discovered that synthetic water had better removal efficiency than field water. Sherene [86] states that the ionic strength of the solution tends to have an impact on the metal ion's ability to adhere to the adsorbent. In this aspect, the metal ion adsorption drops with growing ionic strength in the solution. Real water samples have higher ionic strength than synthetic water because it contains a variety of other ionic pollutants. As a result, the capacity of hardness causing ions to adsorb onto the CSAC is diminished by the presence of other ions.

In addition to calcium salts, seawater may also include other ions, for instance lead and copper divalent ions. At all concentrations assessed, [39]'s study demonstrates that copper favors sodium's affinity for tea leaves, furthermore, low concentrations of calcium and lead also encourage sodium binding for unknown reasons. Due to their higher Lewis acidity (mass/charge ratio), calcium and lead ions compete for adsorption sites at higher concentrations. It has been speculated at lower calcium and lead concentrations; the smaller size of sodium ions makes it easier to undergo adsorption in the presence of these ions.

Thus, the presence of interfering co-ions reduces the effectiveness of eliminating a particular ion. This might be crucial for recovering particular metals or ions with high economic worth. In this context, removing all contaminants (metal or other ions) simultaneously employing a non-specific or non-selective bioadsorbent and limiting the total operations/steps may be advantageous with the goal of remediating water resources. It is also possible to leverage a variety of biosorbents that have distinct specificities and selectivities [30].

Benefits and limitations of bioadsorption for the desalination process

Benefits of bioadsorption processes

Adopting plant-based materials as bioadsorbents is one of the major benefits of bioadsorption procedures. Nature has an abundance of these materials, including coconut husk, rice husk, and coconut coir [8]. In addition to assuring a sustainable supply, this inherent availability helps the bioadsorption method to be more financially viable than other contemporary technologies.

Furthermore, bioadsorption techniques have the benefit of efficiently adsorbing ions that cause salinity in a shorter contact time. Rapid ion exchange and adsorption are made possible on account of their large surface area, porosity, and functional groups. Bioadsorbents can be further enhanced and modified to increase their adsorption capabilities and selectivity in addition to their inherent features using a variety of physical and chemical processes [9].

Additionally, reverse osmosis (RO) water may be efficiently pre-treated using bioadsorption [51]. RO is a commonly employed desalination process; however, due to the presence of dissolved salts and other impurities, it frequently has problems with fouling and scalability. Bioadsorption increases the effectiveness and lifetime of the RO system by decreasing the load on the membranes, which leads to better desalination performance throughout.

Also, utilizing biomaterials as alternative commercial adsorbents viz. coconut coir, rice husk, and coconut husk can prove to be an advantage for the environment. Since these biomaterials are less susceptible to biodegradation, microbes take a longer duration for

the degradation of these materials [87]. Utilizing such materials for desalination delivers a sustainable alternative for waste management as well as water treatment.

Limitation of bioadsorption processes

There are a few disadvantages to bioadsorption that should be taken into account when using it for desalination procedures. One of these is the insufficient supply of bioadsorbents in an easily accessible form in nature [88], which frequently require physical or chemical alterations. Because bioadsorbents are made of plants, there is a risk that color could leech into the solution being treated, necessitating various degrees of treatment for the color-removal process [89].

Additionally, bioadsorbents may have ion-specific adsorption characteristics, which may restrict their capacity to successfully remove certain ions from water [90]. The sustainability of the desalination process is constrained by the difficulty of recycling or discarding spent bioadsorbents. Moreover, the characteristics of natural or synthetical harnessed adsorbents can be influenced by the synthesis processes, external variables, and intended uses, making it difficult to produce bioadsorbents with every attribute required. Finding an efficient and reproducible way to satisfy these demands is, therefore, a significant barrier to producing attractive adsorbents [8].

Lastly, there are relatively few studies emphasizing the significance of modeling engineering design [91], which would provide the link between mechanism identification and engineering application. Understanding and addressing these drawbacks is essential for optimizing and successfully using bioadsorption techniques in desalination applications.

Conclusions

Currently, the state of art technologies employed for salt removal are either costly or require a skilled labor force therefore, the application of bioadsorbents can provide an alternative technology being lucrative and eco-friendly for the elimination of salts from aqueous solutions. However, there is a need for optimization of parameters while utilizing bioadsorptions for desalination technology. This includes the type of bioadsorbent utilized, the surface modification required to increase the bioadsorption capability of the bioadsorbent, variation in pH, contact time, and bioadsorbent dosage that can affect the overall removal efficacy of salts from saline water.

Considering all studies reviewed, the maximum removal efficiency for salinity-causing ions varied from 18 to 98.9% for different bioadsorbents. The optimal pH ranged from 6 to 7 whereas the dosage of the adsorbent varied from 0.1 to 4 g/L, bioadsorbent particle size varied from 0.5 mm to 2.26 mm and contact time varied from 10 min to 4 h. Furthermore, the Freundlich isotherm and pseudo-second-order kinetics were the prevalent models that accurately illustrated the salinity ions equilibrium and isotherm data. The thermodynamic parameters specified that salt ions biosorption on bioadsorbents was endothermic and spontaneous in nature.

It has been evident that naturally occurring low-cost plant-based materials or farm produce wastes have the potential to remove salts ions from water however, very less analyses have been conducted out to actually evaluate the efficiency of these materials for salt removal on field samples. It is essential to consider the influence of other ions on the adsorption capabilities of the bioadsorbents.

The majority of studies published in the literature were lab-scale research. The procedure of ion bioadsorption for desalination and water softening is not yet prepared for industrialized relevance due to technological adversities including scale-up, system setup, system efficacy, etc. The majority of the investigations are carried out in batch studies and thus more supporting experimentation needs to be done in column study to understand the validity of continuous flow on the bioadsorbents employed and their capacity.

Furthermore, the performance of the bioadsorption mechanism is influenced by properties of both bioadsorbent and adsorbate, environment, and operational parameters for instance pH, initial concentration of solute, the presence of other ionic and non-ionic compounds, and so on. As a result, an upgradation of studies is required to assess the efficacy of salt removal on actual seawater samples or brackish water samples and real-time testing of the effectiveness of these treatments.

For softening and desalinating low-salinity water, existing adsorbents are suitable. Besides that, the underlying mechanisms in the bioadsorption of salt ions on various bioadsorbents have received relatively little attention, and much more investigation is required to demonstrate the actual mechanism. However, for industrial use and the desalination of high-salinity water, it is crucial to find, synthesize, modify, or integrate bioadsorbents with greater competence in terms of capacity and resilience.

Abbreviations

BP	Beetroot pulp
SCB	Sugarcane bagasse
GT	Green tea
PM	Peppermint
CM	Chamomile
EC	Electrical conductivity
ACC	Activated coconut coir
TDS	Total dissolved solids
CSAC	Coconut shell activated carbon
WSA	Wheat straw ash
RHA	Rice husk ash

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Authors' contributions

RD conceptualized the study, conducted the review, and presented the data for the first draft of the manuscript written. PS provided guidance and reviewed the manuscript. All authors read and approved the final manuscript.

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