A critical review of biosorption of manganese (Mn²⁺) and nickel (Ni²⁺) ions from aqueous solutions

Afsar Khan^{a,c,*}, Abdul Naeem^a, Nisar Muhammad^b, Shafqat Hussain^c, Ishrat Jamil^c, Irfan Shah^d

^aNational Centre of Excellence in Physical Chemistry, University of Peshawar, Peshawar, Pakistan 25120, Tel. +92 91 9218480; emails: afsarkhan9343@gmail.com (A. Khan), Tel. +92-91-9216766; email: naeeem64@yahoo.com (A. Naeem) ^bDepartment of Environmental Science, Gomal University, 29050, Dera Ismail Khan, Pakistan, Tel. +923008886864; email: nisar5609@gmail.com ^cDepartment of Chemistry, University of Baltistan, Skardu 16250, Pakistan, Tel. +923122301015;

^aDepartment of Chemistry, University of Battistan, Skarau 16250, Pakistan, 1et. +923122301015; email: shafqat.hussain@uobs.edu.pk (S. Hussain), Tel. +923088321909; email: ishrat.jamil@uobs.edu.pk (I. Jamil) ^aDepartment of Chemistry, Abbottabad University of Science and Technology, Pakistan, Tel. +923115819264; email: irfan.shahg2015@gmail.com

Received 21 August 2022; Accepted 25 December 2022

ABSTRACT

Although biosorption is considered a cost-effective, eco-friendly, and straight forward technology to remove toxic metals from aqueous solutions, there are still some gaps that restrain its commercialization. For this purpose, various articles and patents have been published each year to make this technology more economical and effective. We reported a review on the biosorption of manganese ions (Mn²⁺) and nickel ions (Ni²⁺) from aqueous solutions. Various biosorbents have been reported for the effective removal of these toxic ions. These biosorbents include algal biomass, fungal biomass, *Aspergillus niger* and *Saccharomyces*, green tomato husk, corncob biomass, coconut shells, bacteria, Birbira leaves, *Pseudomonas aeruginosa*, maize stalks, crab shell particles, macroalgae *Fucus vesiculosus*, and rice bran. All biosorbents have good capacity of adsorption particularly algal and fungal biomasses. pH study, kinetic investigations, initial concentration, temperature, thermodynamic study and application of isotherms have been evaluated for biosorption of manganese ions (Mn²⁺) and nickel ions (Ni²⁺).

Keywords: Biosorption; Biosorbents; Manganese ions (Mn²⁺) and nickel ions (Ni²⁺); Fungal biomass; Thermodynamics; Isotherms

1. Introduction

Water contamination by toxic heavy metals such as Mn²⁺ and Ni²⁺ ions is one of the main environmental issues humankind is nowadays facing and directly threatens the planet's environmental balance and sustainability of life on earth for future generations. As a consequence, of water pollution about half of the world's population has no easy access to clean fresh drinking water [1,2]. Nickel and manganese are a toxic heavy metals mostly present in water as Ni²⁺ and Mn²⁺ ions. Several industries such as mining, electroplating, nickel and manganese alloys, batteries and steel manufacturing are accountable for release of contaminants into water. The permissible limit of nickel in drinking water is 0.02 mg/L while for manganese it is 0.5 mg/L. High concentration of Ni²⁺ in environment is associated with enzyme inhibition, vomiting, chest pain, dizziness and diarrhea and also causes lung, kidney and skin diseases. Nickel is carcinogenic and affect the deoxyribonucleic acid linkages. Similarly Mn²⁺ damage the central nervous system (CNS) and cause various diseases like manganism (lack of coordination, muscle stiffness, difficulties with swelling tremors, and breathing), liver problems,

^{*} Corresponding author.

learning weakness in children, birth defects, male fertility and low external ears [1,3].

The concentration of nickel and manganese exceeded the permissible level in drinking water. Moreover, nickel and manganese have crossed its permissible limit in drinking water of Palosi Drain of Peshawar, Hayat Abad, Akbarpura, Hasan Abdal, and Gadoon, in Khyber Pakhtoonkhwa province of Pakistan, Kalar Kahar, Kalalanwala, Sialkot city and Kasur, in Punjab and Machar Lake Jamshoro, Sehwan, and Karachi of Sindh province in Pakistan [2]. Development of novel and efficient methods to treat these toxic heavy metals before and after entering to the water body is a pressing need. Biosorption of heavy metals is promising method due to low cost, high efficiency, simple, no formation of toxic side products, and regeneration. Various biosorbents (Tables 1 and 2) such as algal biomass, fungal biomass, Aspergillus niger and Saccharomyces, green tomato husk, corncob biomass, coconut shells, bacteria, birbira leaves, Pseudomonas aeruginosa, maize stalks, crab shell particles, macroalgae Fucus vesiculosus and rice bran have been applied for elimination of heavy metals from water [4]. We are organizing various biosorbents for nickel and manganese removal from aqueous solutions and various external conditions such as pH study, kinetics investigations, initial concentration, temperature, thermodynamic study and application of isotherm have been evaluated for biosorption of manganese ions (Mn²⁺) and nickel ions (Ni²⁺) [5,6].

2. Biosorption of manganese (Mn²⁺)

Bai et al. [7] examined the sorption of Mn^{2+} by *Pseudomonas* sp.H117. Physiochemical characterization, adsorption isotherms and kinetic analysis were evaluated. Chemical Adsorption, ion exchange and electrostatic force of attraction were the sole mechanism. Various kinetic equations were tested to kinetic data and found that pseudo-second-order equation was best fitted to kinetic data. The Langmuir equation has described best the equilibrium data. Thermodynamics parameters proved the process to be spontaneous and endothermic in nature.

Wang et al. [8] reported the Mn²⁺ elimination and oxidation by manganese-oxidizing fungus *Cladosporium halotolerans* strain XM01 showing enhanced uptake and oxidation of soluble Mn²⁺ of 99.8% and 88.3%, respectively. Fixed bed column study of Mn²⁺ elimination demonstrated the oxidation process of Mn²⁺ to Mn⁺³ was the rate-limiting step in metabolic process. The SAED and XRD characterization confirmed that more layers were orderly formed with production of fungal biomass, which might lead to lower its surface area. This study offers mechanism involved into fungal-Mn oxidation and provides theoretical guidance for biomasses in heavy metals removal.

Okoniewska et al. [9] studied the uptake of Mn²⁺ from electrolyte solution on impregnated activated carbon. The sorption was highly pH dependent. The best result was observed for manganese adsorption as compared to iron. They further discussed the complex formation between iron and manganese.

Mane et al. [10] also investigated the biosorption of Mn²⁺ by pre-treated algal biomass. They found greater adsorption capacity of algal biomass as compared to olive cell.

The process was chemisorption in nature upto the temperature range of 35°C and was found physiosorption at higher temperature. The sorption was highly pH dependent and increased with increase in pH.

Parvathi et al. [11] also evaluated studies for the biosorption of Mn^{2+} by *Aspergillus niger* and *Saccharomyces*. The biosorption of Mn^{2+} was dependent upon pH, concentration and dosage amount. Freundlich isotherm was found to be applicable to sorption data. The mechanism of Mn^{2+} adsorption was physiosorption in nature.

Silva et al. [12] also studied the sorption of Mn^{2+} by *Pseudomonas aeruginosa*. The adsorption was pH dependent and the maximum adsorption was found at pH 7. The sorption capacity of *Pseudomonas aeruginosa* was reported to be low. Langmuir model was found to be best fitted with good correlation coefficient.

Liu et al. [13] studied simultaneous removal of manganese, from the copper tailings by a novel magnetic modified biosorbent. The biosorbent was synthesized through an in-situ precipitation method. The biosorption process was pH, time, and particle size dependent, and maximum concentrations released in the eluate were 1.7, 1.8, and 4.1 mg/L under weak acid condition. Various characterization techniques were used for the analysis of surface morphology. Both column and batch adsorption methods were tested for adsorption process. Column experiments showed that higher than 99% of the released Mn could be simultaneously removed by the magnetic modified bagasse. After recycled by a magnet, the magnetic modified bagasse was collected easily and used repeatedly. Because of high efficiency and easy recovery, the used method had great practical application value in removal of potentially toxic elements released from metallic tailings.

Li et al. [14] studied the Mn^{2+} removals by thermally decomposed leaf, as a function of temperature and pH, dose amount. Biosorption of Mn^{2+} was found to enhance with the increment in temperature. The entropy change was found to be negative while the positive enthalpy change was recorded by Li et al. [14].

Hasan et al. [15] investigated the biosorption of Mn^{2+} by isolated bacteria. Different parameters were tested for the sorption of manganese from aqueous solution. Langmuir model was found to be applicable to the sorption data. The maximum sorption was observed at pH 6.5.

Vijayaraghavan et al. [16] used crabbed shell particles for the removal of manganese and the adsorption was found to be pH dependent and the maximum sorption was observed at pH 6. The mechanism of sorption was reported to be micro precipitation. Both pseudo-first and secondorder kinetic models were found to be best fit to the kinetic data. Langmuir model described the equilibrium data with good correlation coefficient (R^2).

García-Mendieta et al. [17] explored the affinity of green tomato husk towards the adsorption of Mn^{2+} . The pseudosecond-order equation was well fitted to the kinetic data. Langmuir model best described the equilibrium data, and the sorption mechanism was found to be ion exchange.

Naeem et al. [2] studied sorption of manganese by *Pleurotus ostreatus* under various conditions. Equilibrium data was explained with the help of adsorption isotherms. Among these isotherms Langmuir model was found to be

more suitable. Various thermodynamic variables were determined and results showed process to be endothermic and spontaneous. The pseudo-second-order kinetics model was found to applicable to kinetic data.

Hasan et al. [18] studied biosorption of Mn²⁺ ions by locally isolated *Bacillus cereus*. Effect of pH, biomass dosage and initial concentration were investigated using the Box– Behnken design. The maximum adsorption was achieved at pH 7. The adsorption capacity was increased by increase of initial concentration of adsorbate concentration. The precipitation of manganese on the surface was confirmed by energy dispersive X-ray, transmission electron microscopy and Fourier-transform infrared.

Raju et al. [5] investigated the biosorption of Mn by *Parthenium Hysteroporous* bud and leaf powder. The effect of contact time, pH, initial concentration were investigated in detail, Temperature effect was investigated in the range of 283–323 K, the surface morphology of the biomaterials were explored by the FTIR, XRD, SEM characterization technique.

Yang et al. [19] reported Mn biosorption by *oleaginous microalgae*. Algae lipid production and heavy metal removal was found a low cost and eco-friendly method for wastewater treatment. *Chlorella minutissima* was found strong resistance to manganese ions under heterotrophic culture condition and effectively eliminated them through extracellular immobilization and intracellular accumulation.

Moreno-Piraján et al. [20] investigated Mn²⁺ removal onto coconut shells. The process was pH dependent and found greater at high pH value. Pseudo-second-order equation and Langmuir isotherm were observed to be well fitted to the experimental data.

Gialamouidis et al. [21] observed that the adsorption of Mn^{2+} by *Pseudomonas* sp. increased with the increase in temperature. Langmuir model described equilibrium data with good correlation coefficient (R^2). The pseudo-second-order model was observed to be well fitted to the kinetic data. The positive value of enthalpy showed the endothermicity of the process. The desorption study revealed that 88% of the biomass can be regenerated safely.

Kamarudzaman et al. [22] reported Mn biosorption by *Pleurotus ostreatus* mushroom in fixed-bed column, effects of bed height, flow rate and initial concentration were investigated. The breakthrough time was found to increase with the decrease in flow rate and initial concentration of heavy metal. The EDX and FTIR were performed before and after adsorption to confirm the manganese adsorption on adsorbent surface.

Amorim et al. [23] reported Manganese Mn^{2+} sorption by *Meyerozyma caribbica* and *Meyerozyma guilliermondii* strains. The study was conducted to use yeast for effective capturing of the Mn^{2+} ions from aqueous solutions. Various Physiochemical investigations were performed to characterize the surface morphology of the biosorbent. Yeast was found to be suitable biosorbent for manganese removal.

2.1. Effect of pH on Mn²⁺ biosorption

Li et al. [14] studied the effect of pH on manganese removal by thermally decomposed leaf. The sorption was found to increase with increase in pH and the precipitation of Mn^{2+} occurred at pH 7. The increase in the uptake of Mn^{2+} with pH was attributed to the electrostatic interaction between the negatively charged surface and metal cations.

Gialamouidis et al. [21] evaluated adsorption of Mn²⁺ at varying pH using *Pseudomonas* sp. It was observed that pH played a significant role in recovery of Mn²⁺ from water. Adsorption was found to be high at high pH ranging from 2 to 6. Beyond pH 6 a decrease in adsorption was observed due to precipitation of Mn(OH)₂. It was also noted that in acidic pH range, the surface is positively charged which results in the repulsion between the metal cations and positively charged surface.

Hasan et al. [15] studied the biosorption of Mn^{2+} by isolated bacteria. Adsorption was strongly pH dependent and was high at high pH value of the solution. Maximum uptake of Mn^{2+} was reported at pH 9.

Tsekova et al. [24] studied the adsorption of manganese by free and immobilized cells of *Aspergillus niger*. Tsekova et al. reported a significant effect of pH on adsorption. They reported that sorption increased with increase in pH in the range of 3–7.5 and beyond pH 7.5 the sorption of Mn²⁺ decreased due to its precipitation.

Mengistie et al. 2012 [25] reported the effect of pH and temperature on the uptake of Mn²⁺ by Birbira leaves. The pH effect was studied in pH range 2–7. The maximum sorption was observed at pH 4 while at lower pH adsorption was decreased because of repulsion between surface and manganese ions.

Parvathi et al. [11] also investigated the pH effect on Mn²⁺ sorption by *Aspergillus niger* and *Saccharomyces cerevisiae*. They observed that pH has significant role on the sorption process. The sorption was substantially increased with increasing pH in the range 2–7.

Silva et al. [12] evaluated adsorption of Mn^{2+} by *Pseudomonas aeruginosa*. The study revealed that the process was pH dependent and a decrease in adsorption was observed with increasing pH. Due to precipitation at higher pH (pH > 7) sorption was observed to be minimum as it was replaced by precipitation.

Moreno-Piraján et al. [20] studied the sorption of Mn, Fe, Ni and Cu ions from wastewater onto activated carbon. The pH study was carried out in the pH range of 2–8. Maximum adsorption was recorded at pH 5.8 and solubility product (K_{sp}) was confirmed by precipitation of metal hydroxide at pH > 6. Sorption of Mn²⁺ was increased with increase in the pH.

2.2. Effect of temperature on Mn^{2+} biosorption

Mengistie et al. [25] evaluated the influence of temperature on elimination of Mn^{2+} by Birbira leaves at a constant pH. The increase in sorption with at high temperature was owing to ionic mobility, metal ions diffusion and enlargement of pore size of adsorbent. Moreover the thermodynamic study showed the endothermic nature of process.

Youngwilai et al. [26] reported manganese adsorption by *Streptomyces violarus* biochar. The results demonstrated that oxygen containing functional group of modified biochar was responsible for manganese elimination. Kinetic data followed pseudo-second-order model and Langmuir model was applicable with the maximum adsorption capacity of 1.2 mg/g. The highest elimination efficiency was 78% during adsorption process. The advanced synchrotron analyses confirmed that manganese adsorption was because of the synergistic combination of manganese with sorbent surface.

Jagung [27] reported the uptake of Mn²⁺ from water as a function of temperature by maize stalks. Sorption was decreased from 39% to 13% in the range of 25°C–55°C. The process was exothermic and spontaneous in nature. They concluded that, it may be due to destruction of some active sites at high temperature.

2.3. Kinetic studies of Mn^{2+} biosorption

Vijayaraghavan et al. [16] studied time course profile for the adsorption of Mn²⁺ on crab shell particles. Adsorption kinetic was very fast in the start then decreased and equilibrium was established within 8 h. Almost 90% adsorption was completed in 60 min. The initial quick uptake of Mn²⁺ was because of active sites on crab shell surface. The kinetic data was verified by using several models. They observed that the Elovich model was the more suitable.

Moreno-Piraján et al. [20] examined the effects of time for Mn²⁺ adsorption on activated carbon. Equilibrium was rapidly established in 8 min. The data was subjected to several kinetic models like pseudo-first and second-order equations. Morino et al. claimed that pseudo-second-order model was applicable with good correlation coefficient.

Li et al. [14] studied the kinetics of Mn²⁺ adsorption on thermally decomposed leaf. It was concluded that adsorption rate was initially rapid due to availability of strong bonding sites. However, with laps of time the sorption capacity was decreased due to weak bonding sites. The kinetic data was analyzed by pseudo-second-order kinetic model.

The effect of time on removal of Mn^{2+} by *Pseudomonas* sp. at 299 K with different initial metal ions concentration was undertaken by [21]. The equilibrium time for Mn^{2+} showed nondependent on the initial ion concentration and in all cases equilibrium was established in 10 min. The adsorption was observed quickly on the bare surface of the biosorbent and then a slower uptake of Mn^{2+} was observed.

Mengistie et al. [25] used activated carbon of Birbira for the decontamination of water from manganese. The kinetic investigation demonstrated that that the uptake was initially very quick and then decreased with laps of time. The rapid uptake was due to the available bare surface sites for metal ions sorption and Equilibrium was attained after 2 h.

3. Biosorption of nickel (Ni2+) ions

Krishnan et al. [31] studied (Ni^{2+}) elimination onto activated carbon obtained from sugarcane bagasse. The sorption of (Ni^{2+}) under various time intervals confirmed the equilibrium time at 4 h. The (Ni^{2+}) uptake was increased with rise in pH and temperature. Both pseudo-first and pseudo-second-order equations were best applicable to the kinetic data. The rate constant values were observed to decrease with the increase in nickel concentration. It was also revealed 93% desorption of (Ni^{2+}) occur with 0.01 M HCl. The Langmuir

isotherm was applied and showed well fit to the equilibrium data.

Moreira et al. [32] reported biosorption of (Ni²⁺) ions by macroalgae *vesiculosus* biosorbent. Biosorbent was characterized by various physiochemical technique, Kinetic, equilibrium and thermodynamic studies were performed. All isotherms followed by experimental data except Freundlich isotherm. Thermodynamic investigation confirmed the spontaneous and exothermic nature of the adsorption process.

Kulkarni et al. [33] reported biosorption of Ni by *Bacillus laterosporus*. The biosorption was examined under the contact time, effect of pH, initial metal ion concentration and biosorbent dosage. Equilibrium was established at 120 min. Langmuir adsorption isotherm was applicable to the experimental data. Kinetic study confirmed the process followed pseudo-second-order equation. Thermodynamic study showed confirmed the endothermic process. The surface characteristics of laterosporus biomass before and after metal biosorption were analyzed by using scanning electron microscope (SEM) with energy dispersive X-ray spectroscopy (EDAX) to study the changes in surface morphology and elemental constitution of the adsorbent.

Zafar et al. [34] investigated biosorption of (Ni²⁺) ions from aqueous solutions by modified rice bran as a biosorbent. The kinetic data was tested by various kinetic equations such as pseudo first and pseudo-second-order equations. The Freundlich and Langmuir models were tested to the equilibrium data and fitted well the Langmuir isotherm. The maximum sorption capacity of for (Ni²⁺) was found to be 153 mg/g. The regeneration experiment confirmed the reuse of adsorbent.

Çelebi et al. [35] reported nickel by brewed tea waste. The pH effect, adsorbent amount and contact time were evaluated throughout the process. The adsorption was found to decrease with increase in pH and increase with increase of other parameters. The optimum pH was between 5.0 for adsorption process. Equilibrium times 30 min was required for the adsorption of (Ni²⁺) ions. The maximum adsorption capacities were calculated as 1.163 mg/g, for Ni adsorption by fitting the equilibrium data to the Langmuir model.

Chanda et al. [36] examined nickel adsorption by using mahogany sawdust. The biosorbent material was characterized by FTIR spectroscopy, SEM/EDX analysis. pH Effect, biomass dosage, temperature and contact time were investigated in batch adsorption experiments Pseudo-secondorder equation and Langmuir model were best applicable to the experimental data. Thermodynamic variable confirmed that adsorption process was endothermic, spontaneous and random in nature.

Gialamouidis et al. [21] studied removal Ni²⁺ from aqueous solutions by *Pseudomonas* sp. cells. Experiments were conducted at various conditions of temperature, pH and time. pH plays important role in the adsorption process. The maximum adsorption was occurred at pH 5 and 6 for *Pseudomonas* sp. and *S. xylosus*, respectively. Desorption was carried out in 0.1 M HNO₃. The results showed that adsorption was decreased at high adsorbent dose.

Subbaiah et al. [37] reported biosorption of Ni²⁺ from aqueous solutions by *Acacia leucocephala*. The biosorption

process was mainly dependent on pH of medium. Various kinetic models like (pseudo-first and pseudo-second-order) were used to test the kinetic data. The pseudo-second-order kinetic model was found to be best fit to the kinetic data. Similarly, Langmuir model was best applicable to equilibrium data. Thermodynamics variables confirmed the endo-thermic and spontaneous nature of the process.

Reddy et al. [38] used *Moringa oleifera* bark for elimination of Ni²⁺ ions from aqueous solution. The material was characterized by SEM, EDX, FTIR and XRD. Experimental data was tested by different sorption models such as Langmuir, Freundlich, D.R model and Timken isotherms. The Langmuir equation was best fitted to the equilibrium data. Pseudosecond-order equation was applicable with correlation coefficient > 0.98. Desorption experiments were conducted in 0.1 M HCl which resulted 98% nickel recovery from the surface. The thermodynamic variables confirmed the endothermic and spontaneous nature of the process.

Gonsalvesh et al. [39] reported Ni^{2_+} removals by polystyrene based activated carbons. Steam activated carbon showed Ni^{2_+} removals at various conditions. Ni^{2_+} ions adsorption mechanism was found to be cation exchange at pH range of 4–8. The kinetics of Ni^{2_+} is best explained by a pseudosecond-order equation. Langmuir model best explained the equilibrium data.

Kurniawan et al. [40] concluded adsorption study on removal of Ni²⁺ by cassava peel waste as environmental friendly biosorbent. The physiochemical characterization was done by FTIR, EDX, SEM, XPS and XRD. Pseudosecond-order equation was applicable, and the process was chemisorption's in nature.

Mahmood et al. [1] examined the equilibrium and kinetics study for adsorption of Ni²⁺ ions by *Pleurotus ost-reatus*. Experiments were conducted with respect to pH, temperature and biomass dosage. The sorption was found to be decreased with increase in pH, temperature and concentration while the sorption was decreased with increase in biomass dosage. It was observed that temperature has insignificant effect on the biosorption of Ni²⁺ as compared to pH. Pseudo first order kinetic model was well fitted to the kinetic data. Desorption studies were carried out in 0.01 M H₂SO₄ and the result showed the biosorbents can be reused five times in adsorption desorption process.

Bermúdez et al. [41] investigated nickel sorption using *Sargassum muticum* and *Gracilaria caudata*. pH 3 was the optimum pH for adsorption process. The data were tested by various models like Langmuir and Freundlich. Both models were found to be best applicable to the sorption data. The kinetic data were subjected to the pseudo-second-order and intra particle diffusion equations. Process was endothermic in nature and enhanced with increase in temperature.

Sinyeue et al. [6] reported the elimination of Ni²⁺ ions by natural and modified *Pinus caribaea* Morelet sawdust. The sorbent was characterized by FTIR and SEM. Several conditions such as contact time, size of particles, initial metal, pH and biomass dosage, desorption conditions and reusability were evaluated on natural biomass. The maximum sorption occurred at pH 5. Equilibrium was achieved in 2 h. Freundlich isotherms were found to be best fit to equilibrium data. The removal was enhanced at high temperature. The adsorbent was found low cost, environmentally friendly. To increase adsorption capacity the adsorbent was modified with acidic and oxidative treatment.

3.1. Effect of pH on Ni²⁺ biosorption

Joshi et al. [46] reported pH effect on uptake of Ni²⁺ and Cu²⁺ by various semiconducting materials. The result confirmed that adsorption was declined at high pH in the range 3–5. They investigated that maximum sorption was occurred at pH 4 whereas adsorption was minimum at pH 3.

Tahir et al. [47] investigated Ni²⁺ eliminations from industrial samples by Bacillus species. The process was pH dependent and was found to high at high pH from 4 to 8.

Reddy et al. [38] investigated effect of pH on Ni²⁺ adsorption from water by *Moringa oleifera* bark. The results showed that adsorption was increased with increase in pH in the range 3–8. The PZC of the sorbent was recorded to be 4.2 by using salt addition method.

Lalhruaitluanga et al. [48] investigated the pH effect while using non activated and activated charcoals for the removal of Ni²⁺ and Zn²⁺ from aqueous solutions. The results showed that higher pH was favorable to the adsorption process. The lower adsorption in acidic pH range was due to the competition amid hydrogen and metal ions towards the surface. The optimum pH for metal sorption was noted at pH 5.

Cayllahua and Torem [49] reported the pH effect on the adsorption of nickel and aluminum ions from aqueous solution. The sorption was highly pH dependent and maximum adsorption was observed at pH 5.

Aikpokpodion et al. [50] investigated the adsorption of Ni²⁺ from water using waste tea materials. The sorption of Ni²⁺ was negligible at lower pH because of metal and hydrogen ions competition towards the surface sites. The maximum adsorption was observed at pH 5 and at higher pH the adsorption was found to be decreased due to precipitation of Ni (OH)₂.

Wierzba and Latała [51] reported the biosorption of Ni²⁺ by bacterial biomass. The results showed that cation affinity towards the surface depends upon the pH of medium. The adsorption was increased with increase in the pH and maximum adsorption was occurred at pH 7. They observed that adsorption of metal ions was highly influenced by protonation and deprotonation of surface depending upon the pH of medium.

3.2. Temperature effect on Ni²⁺ biosorption

Öztürk et al. [52] studied the effect of temperature while studying the removal of Ni²⁺ and Cu²⁺ions onto Streptomyces coelicolor. It was observed that temperature has little effect on the sorption process. Maximum adsorption occurred in the temperature range 20°C–30°C. The sorption was found to reduce with rise in temperature of the system.

Bansal et al. [53] investigated the effect of temperature on adsorption of Ni²⁺ by agriculture waste. The result showed the process was endothermic in nature. Various characterization techniques like SEM, EDX, XRD and FTIR showed the porous structure of adsorbent and the metal ions were diffused in the pores of adsorbent at high temperature.

Tabla	1
Table	T

Various biosorbents for removal of Mn	²⁺ from aqueous solution
---------------------------------------	-------------------------------------

Biosorbents	Sorption capacity (mg/g) Mn ²⁺	References
Aspergillus niger	19.34	Parvathi et al. [11]
Pseudomonas aeruginosa	22.39	Silva et al. [12]
Magnetic modified biosorbent	13.1	Liu et al. [13]
Saccharomyces cerevisiae	22.5	Fadel et al. [28]
Bombax malabaricum	0.28	Emmanuel et al. [29]
Natural clay	10	Eba et al. [30]

Similar temperature effect was investigated by Tahir et al. for biosorption of Ni²⁺ from industrial influents by Bacillus species. No significant effect of temperature on the sorption process was observed.

Kakalanga et al. [54] studied the effect of temperature during screening of agricultural waste for Ni²⁺ adsorption. The temperature study was carried out in the range of 295–333 K. The sorption was exothermic in the temperature range 295 to 303 K. However, no significant effect of temperature was observed in the range 303–323 K. The results confirmed the physical nature of the process.

Singh et al. [55] studied adsorption of Ni^{2+} from by an indigenous adsorbent peanut shell. It was noted that temperature has a prominent influence on biosorption in the range of 25°C–75°C and indicating that the endothermicity of the process.

Suazo-Madrid et al. [56] reported the effect of temperature on Ni²⁺ biosorption by *Rhodotorula glutinis*. The nature of the adsorption process was observed to be endothermic. It was due to the reason that rise in temperature resulted in the increase of the active sites and diffusion of ions into the pores of the surface.

3.3. Kinetic studies of Ni²⁺ biosorption

Chen et al. [57] studied the effect of time on the Ni²⁺ adsorption by metal-imprinted chitosan at pH 5 and reported rapid initial rate of adsorption during the first 60 min and adsorption equilibrium was maintained in 180 min. The kinetic data were applied to pseudo first and second-order kinetic models. It was reported by them that pseudo-second-order kinetic model fitted well with higher value of the correlation coefficient (R^2).

Rodrigues et al. [58] removed Ni²⁺ ions from water by using dry biomass of Arthrospira and reported the effect of time on the adsorption process. The experimental results were tested using pseudo first and second-order kinetic models. The pseudo-second-order kinetic model was found to be more suitable. It was observed that sorption was proportional to the active sites and initially rapid adsorption was observed.

Bhatnagar and Minocha [59] studied kinetics of the Ni²⁺ sorption by *Punica granatum* peel. The result showed that adsorption rate was rapid in the start and 50% uptake was recorded within 2 h. Equilibrium was achieved in 7 h and the data was tested by pseudo first, pseudo-second and intra particles diffusion models. It was observed that the

Table 2

Various biosorbents for removal of Ni2+ from aqueous solution

Biomass	Sorption capacity (mg/g) Ni(II)	References
Ulva reticulata	46.5	[42]
Algae Cystoseira	18	[43]
Carob shells	13.5	[44]
Dry residual biomasses	21.3	[45]

adsorption process was described more suitably by pseudo-second-order kinetic model.

Hannachi [60] carried out the kinetic study of Ni²⁺ adsorption by finely divided waste sludge. The pseudo first and pseudo-second-order kinetic models were used to evaluate the kinetic data. The rate constant was calculated from both models and the pseudo-second-order kinetic model was justified for the interpretation of the kinetic data.

4. Conclusion

In the current review paper various biosorbents have been organized for effective removal of manganese ions (Mn^{2+}) and nickel ions (Ni^{2+}) from aqueous solutions. All biosorbents have good capacity of adsorption particularly algal and fungal biomasses. Various eco-friendly parameters have been evaluated and its data were interpreted. The equilibrium data were well interpreted by adsorption isotherm. Biosorption technology need more attention and should be applied on industrial scale. The application of biosorption on industrial scale has not been well explored. All these studies make possible the current knowledge about biosorption that is enough to provide a solid base that allows its use to be extended.

Acknowledgement

The authors acknowledge the National Centre of Excellence in Physical Chemistry (NCEPC), University of Peshawar, 25120 Pakistan and Higher Education Commission (HEC) Pakistan for research support.

Conflict of interest

The authors declare no conflict of interest.

156

References

- T. Mahmood, A. Khan, A. Naeem, M. Hamayun, M. Muska, M. Farooq, F. Hussain, Adsorption of Ni(II) ions from aqueous solution onto a fungus *Pleurotus ostreatus*, Desal. Water Treat., 57 (2016) 7209–7218.
- [2] A. Naeem, A. Khan, T. Mahmood, M. Muska, S. Ud Din, M.S. Khan, M. Hamayun, M. Waseem, Kinetics, equilibrium and thermodynamic studies of Mn(II) biosorption from aqueous solution onto *Pleurotus ostreatus*, J. Chem. Soc. Pak., 36 (2014) 788.
- [3] M. Mon, R. Bruno, E. Tiburcio, M. Viciano-Chumillas, L.H.G. Kalinke, J. Ferrando-Soria, D. Armentano, E. Pardo, Multivariate metal–organic frameworks for the simultaneous capture of organic and inorganic contaminants from water, J. Am. Chem. Soc., 141 (2019) 13601–13609.
- [4] A. Khan, A. Naeem, T. Mahmood, B. Ahmad, Z. Ahmad, M. Farooq, T. Saeed, Mechanistic study on methyl orange and congo red adsorption onto polyvinyl pyrrolidone modified magnesium oxide, Int. J. Environ. Sci. Technol., 19 (2022) 2515–2528.
- [5] C.A. Raju, N. Yugandhar, S.S. Naidu, C. Beena, M.T. Bai, Removal of manganese from synthetic waste waters with *Parthenium Hysteroporous* bud and leaf powder and optimization using Artificial Neural Networks and Response Surface Methodology, Mater. Today Proc., 42 (2021) 851–861.
- [6] C. Sinyeue, T. Garioud, M. Lemestre, M. Meyer, F. Brégier, V. Chaleix, V. Sol, N. Lebouvier, Biosorption of nickel ions Ni²⁺ by natural and modified *Pinus caribaea* Morelet sawdust, Heliyon, 8 (2022) e08842, doi: 10.1016/j.heliyon.2022.e08842.
- [7] Y. Bai, J. Su, Q. Wen, G. Li, L. Xue, T. Huang, Removal of tetracycline by denitrifying Mn(II)-oxidizing bacterium *Pseudomonas* sp.H117 and biomaterials (BMO and MBMO): efficiency and mechanisms, Bioresour. Technol., 312 (2020) 123565, doi: 10.1016/j.biortech.2020.123565.
- [8] M. Wang, Z. Xu, B. Dong, Y. Zeng, S. Chen, Y. Zhang, Y. Huang, X. Pei, An efficient manganese-oxidizing fungus *Cladosporium halotolerans* strain XM01: Mn(II) oxidization and Cd adsorption behavior, Chemosphere, 287 (2022) 132026, doi: 10.1016/j. chemosphere.2021.132026.
- [9] E. Okoniewska, J. Lach, M. Kacprzak, E. Neczaj, The trial of regeneration of used impregnated activated carbons after manganese sorption, Desalination, 223 (2008) 256–263.
- [10] P. Mane, A. Bhosle, C. Jangam, Effect of pretreatment of algal biomass on bioadsorption of chromium from aqueous solution, Res. J. Chem. Environ., 15 (2011) 271–274.
- [11] K. Parvathi, R. Naresh Kumar, R. Nagendran, Biosorption of manganese by Aspergillus niger and Saccharomyces cerevisiae, World J. Microbiol. Biotechnol., 23 (2007) 671–676.
- [12] R.M.P. Silva, A.Á. Rodríguez, J.M.G.M. De Oca, D.C. Moreno, Biosorption of chromium, copper, manganese and zinc by *Pseudomonas aeruginosa* AT18 isolated from a site contaminated with petroleum, Bioresour. Technol., 100 (2009) 1533–1538.
- [13] J. Liu, R. Zhou, J. Yu, L. Guo, X. Li, C. Xiao, H. Hou, R. Chi, G. Feng, Simultaneous removal of lead, manganese, and copper released from the copper tailings by a novel magnetic modified biosorbent, J. Environ. Manage., 322 (2022) 116157, doi: 10.1016/j.jenvman.2022.116157.
- [14] Z. Li, S. Imaizumi, T. Katsumi, T. Inui, X. Tang, Q. Tang, Manganese removal from aqueous solution using a thermally decomposed leaf, J. Hazard. Mater., 177 (2010) 501–507.
- [15] H. Hasan, S. Abdullah, N. Kofli, S. Kamaruddin, Biosorption of manganese in drinking water by isolated bacteria, J. Appl. Sci., 10 (2010) 2653–2657.
- [16] K. Vijayaraghavan, H.Y.N. Winnie, R. Balasubramanian, Biosorption characteristics of crab shell particles for the removal of manganese(II) and zinc(II) from aqueous solutions, Desalination, 266 (2011) 195–200.
- [17] A. García-Mendieta, M.T. Olguín, M. Solache-Ríos, Biosorption properties of green tomato husk (*Physalis philadelphica* Lam) for iron, manganese and iron–manganese from aqueous systems, Desalination, 284 (2012) 167–174.

- [18] H.A. Hasan, S.R.S. Abdullah, N.T. Kofli, S.J. Yeoh, Interaction of environmental factors on simultaneous biosorption of lead and manganese ions by locally isolated *Bacillus cereus*, J. Ind. Eng. Chem., 37 (2016) 295–305.
- [19] J. Yang, J. Cao, G. Xing, H. Yuan, Lipid production combined with biosorption and bioaccumulation of cadmium, copper, manganese and zinc by oleaginous microalgae *Chlorella minutissima* UTEX2341, Bioresour. Technol., 175 (2015) 537–544.
- [20] J.C. Moreno-Piraján, V.S. Garcia-Cuello, L. Giraldo, The removal and kinetic study of Mn, Fe, Ni and Cu ions from wastewater onto activated carbon from coconut shells, Adsorption, 17 (2011) 505–514.
- [21] D. Gialamouidis, M. Mitrakas, M. Liakopoulou-Kyriakides, Equilibrium, thermodynamic and kinetic studies on biosorption of Mn(II) from aqueous solution by *Pseudomonas* sp., *Staphylococcus xylosus* and *Blakeslea trispora* cells, J. Hazard. Mater., 182 (2010) 672–680.
- [22] A.N. Kamarudzaman, T.C. Chay, A. Amir, S.A. Talib, Biosorption of Mn(II) ions from aqueous solution by *Pleurotus* spent mushroom compost in a fixed-bed column, Procedia Soc. Behav. Sci., 195 (2015) 2709–2716.
- [23] S.S. Amorim, F.A.D. Ruas, N.R. Barboza, V.G. de Oliveira Neves, V.A. Leao, R. Guerra-Sa, Manganese (Mn²⁺) tolerance and biosorption by *Meyerozyma guilliermondii* and *Meyerozyma caribbica* strains, J. Environ. Chem. Eng., 6 (2018) 4538–4545.
- [24] K. Tsekova, D. Todorova, S. Ganeva, Removal of heavy metals from industrial wastewater by free and immobilized cells of *Aspergillus niger*, Int. Biodeterior. Biodegrad., 64 (2010) 447–451.
- [25] A.A. Mengistie, T.S. Rao, A.P. Rao, Adsorption of Mn(II) ions from wastewater using activated carbon obtained from birbira (*Militia ferruginea*) leaves, Global J. Sci. Front. Res., 12 (2012) 5–12.
- [26] A. Youngwilai, P. Kidkhunthod, N. Jearanaikoon, J. Chaiprapa, N. Supanchaiyamat, A.J. Hunt, Y. Ngernyen, T. Ratpukdi, E. Khan, S. Siripattanakul-Ratpukdi, Simultaneous manganese adsorption and biotransformation by *Streptomyces violarus* strain SBP1 cell-immobilized biochar, Sci. Total Environ., 713 (2020) 136708, doi: 10.1016/j.scitotenv.2020.136708.
- [27] P.T. Jagung, Removal of Zn(II), Cd(II) and Mn(II) from aqueous solutions by adsorption on maize stalks, Malays. J. Anal. Sci., 15 (2011) 8–21.
- [28] M. Fadel, N.M. Hassanein, M.M. Elshafei, A.H. Mostafa, M.A. Ahmed, H.M. Khater, Biosorption of manganese from groundwater by biomass of *Saccharomyces cerevisiae*, HBRC J., 13 (2017) 106–113.
- [29] K. Emmanuel, K. Ramaraju, K.S. Rao, Removal of Mn(II) from aqueous solutions using bombax malabaricum fruit shell substrate, E-J. Chem., 4 (2007) 419–427.
- [30] F. Eba, S. Gueu, A. Eya'A-Mvongbote, J. Ondo, B. Yao, N.J. Ndong, B. Kouya, Evaluation of the absorption capacity of the natural clay from Bikougou (Gabon) to remove Mn(II) from aqueous solution, Int. J. Eng. Sci. Technol., 2 (2010) 5001–5016.
- [31] K.A. Krishnan, K. Sreejalekshmi, R. Baiju, Nickel(II) adsorption onto biomass based activated carbon obtained from sugarcane bagasse pith, Bioresour. Technol., 102 (2011) 10239–10247.
- [32] V.R. Moreira, Y.A.R. Lebron, L.C. Lange, L.V.S. Santos, Simultaneous biosorption of Cd(II), Ni(II) and Pb(II) onto a brown macroalgae *Fucus vesiculosus*: mono- and multicomponent isotherms, kinetics and thermodynamics, J. Environ. Manage., 251 (2019) 109587, doi: 10.1016/j. jenvman.2019.109587.
- [33] R.M. Kulkarni, K.V. Shetty, G. Srinikethan, Cadmium(II) and nickel(II) biosorption by *Bacillus laterosporus* (MTCC 1628), J. Taiwan Inst. Chem. Eng., 45 (2014) 1628–1635.
- [34] M.N. Zafar, R. Nadeem, M.A. Hanif, Biosorption of nickel from protonated rice bran, J. Hazard. Mater., 143 (2007) 478–485.
- [35] H. Çelebi, G. Gök, O. Gök, Adsorption capability of brewed tea waste in waters containing toxic lead(II), cadmium(II), nickel(II), and zinc(II) heavy metal ions, Sci. Rep., 10 (2020) 1–12.
- [36] R. Chanda, A.H. Mithun, M. Abu Hasan, B.K. Biswas, Nickel removal from aqueous solution using chemically treated

mahogany sawdust as biosorbent, J. Chem., 2021 (2021) 4558271, doi: 10.1155/2021/4558271.

- [37] M.V. Subbaiah, Y. Vijaya, N.S. Kumar, A.S. Reddy, A. Krishnaiah, Biosorption of nickel from aqueous solutions by *Acacia leucocephala* bark: kinetics and equilibrium studies, Colloids Surf., B, 74 (2009) 260–265.
- [38] D.H.K. Reddy, D. Ramana, K. Seshaiah, A. Reddy, Biosorption of Ni(II) from aqueous phase by *Moringa oleifera* bark, a low cost biosorbent, Desalination, 268 (2011) 150–157.
- [39] L. Gonsalvesh, S. Marinov, G. Gryglewicz, R. Carleer, J. Yperman, Preparation, characterization and application of polystyrene based activated carbons for Ni(II) removal from aqueous solution, Fuel Process. Technol., 149 (2016) 75–85.
- [40] A. Kurniawan, A.N. Kosasih, J. Febrianto, Y.-H. Ju, J. Sunarso, N. Indraswati, S. Ismadji, Evaluation of cassava peel waste as lowcost biosorbent for Ni-sorption: equilibrium, kinetics, thermodynamics and mechanism, Chem. Eng. J., 172 (2011) 158–166.
- [41] Y.G. Bermúdez, I.L.R. Rico, O.G. Bermúdez, E. Guibal, Nickel biosorption using *Gracilaria caudata* and *Sargassum muticum*, Chem. Eng. J., 166 (2011) 122–131.
- [42] K. Vijayaraghavan, J. Jegan, K. Palanivelu, M. Velan, Biosorption of copper, cobalt and nickel by marine green alga *Ulva reticulata* in a packed column, Chemosphere, 60 (2005) 419–426.
- [43] M. Khajavian, D.A. Wood, A. Hallajsani, N. Majidian, Simultaneous biosorption of nickel and cadmium by the brown algae *Cystoseria indica* characterized by isotherm and kinetic models, Appl. Biol. Chem., 62 (2019) 1–12.
- [44] F. Bensafiddine, M. Benalia, A. Hadj Seyd, M. Djedid, C. Ad, Z.B. Amar, H. Elmsellem, Biosorption of heavy metals (copper, nickel) and dye (methylene blue) from aqueous solution onto southern Algerian carob shells, Morrocan J. Chem., 8 (2020) 2638–2646.
- [45] A. Herrera-Barros, C. Tejada-Tovar, Á.D. González-Delgado, Green nanoparticle-aided biosorption of nickel ions using four dry residual biomasses: a comparative study, Sustainability, 14 (2022) 7250, doi: 10.3390/su14127250.
- [46] K.M. Joshi, B.N. Patil, D.S. Shirsath, V.S. Shrivastava, Photocatalytic removal of Ni(II) and Cu(II) by using different semiconducting materials, Adv. Appl. Sci. Res., 2 (2011) 445–454.
- [47] A. Tahir, R. Shehzadi, B. Mateen, S. Univerdi, O. Karacoban, Biosorption of nickel(II) from effluent of electroplating industry by immobilized cells of *Bacillus* species, Eng. Life Sci., 9 (2009) 462–467.

- [48] H. Lalhruaitluanga, M. Prasad, K. Radha, Potential of chemically activated and raw charcoals of *Melocanna baccifera* for removal of Ni(II) and Zn(II) from aqueous solutions, Desalination, 271 (2011) 301–308.
- [49] J. Cayllahua, M. Torem, Biosorptive flotation of nickel and aluminum ions from aqueous solution, Desalination, 279 (2011) 195–200.
- [50] P. Aikpokpodion, R. Ipinmoroti, S. Omotoso, Biosorption of nickel(II) from aqueous solution using waste tea (*Camella cinencis*) materials, Am.-Eurasian J. Toxicol. Sci., 2 (2010) 72–82.
- [51] S. Wierzba, A. Latała, Biosorption lead(II) and nickel(II) from an aqueous solution by bacterial biomass, Pol. J. Chem. Technol., 12 (2010) 72–78.
- [52] A. Öztürk, T. Artan, A. Ayar, Biosorption of nickel(II) and copper(II) ions from aqueous solution by *Streptomyces coelicolor* A3 (2), Colloids Surf., B, 34 (2004) 105–111.
- [53] M. Bansal, D. Singh, V. Garg, P. Rose, Use of agricultural waste for the removal of nickel ions from aqueous solutions: equilibrium and kinetics studies, Int. J. Civ. Eng. Technol., 418 (2009) 763–776.
- [54] S.J. Kakalanga, X.B. Jabulani, O.B. Olutoyin, O.O. Utieyin, Screening of agricultural waste for Ni(II) adsorption: kinetics, equilibrium and thermodynamic studies, Int. J. Phys. Sci., 7 (2012) 2525–2538.
- [55] R.S. Singh, V.K. Singh, P.N. Tiwari, U.N. Singh, Y.C. Sharma, An economic removal of Ni(II) from aqueous solutions using an indigenous adsorbent, Open Environ. Eng. J., 2 (2009) 30–36.
- [56] A. Suazo-Madrid, L. Morales-Barrera, E. Aranda-García, E. Cristiani-Urbina, Nickel(II) biosorption by *Rhodotorula glutinis*, J. Ind. Microbiol. Biotechnol., 38 (2011) 51–64.
 [57] C.-Y. Chen, C.-Y. Yang, A.-H. Chen, Biosorption of Cu(II), Zn(II),
- [57] C.-Y. Chen, C.-Y. Yang, A.-H. Chen, Biosorption of Cu(II), Zn(II), Ni(II) and Pb(II) ions by cross-linked metal-imprinted chitosans with epichlorohydrin, J. Environ. Manage., 92 (2011) 796–802.
- [58] M.S. Rodrigues, L.S. Ferreira, J.C.M. de Carvalho, A. Lodi, E. Finocchio, A. Converti, Metal biosorption onto dry biomass of *Arthrospira (Spirulina) platensis* and *Chlorella vulgaris*: multimetal systems, J. Hazard. Mater., 217 (2012) 246–255.
- [59] A. Bhatnagar, A.K. Minocha, Biosorption optimization of nickel removal from water using *Punica granatum* peel waste, Colloids Surf., B, 76 (2010) 544–548.
- [60] Y. Hannachi, Nickel biosorption by finely ground waste sludge, J. Environ. Eng. Landscape Manage., 19 (2011) 208–214.