

Review

**MECHANISMS AND FACTORS INFLUENCING Ni(II) BIOSORPTION BY
BACTERIAL EXOPOLYSACCHARIDES: A REVIEW**

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Abstract

This review paper analyses the biosorption of Ni²⁺ ion by using unmodified bacterial exopolysaccharides (EPS), based on data from available literature, while this system has been investigated less compared to other heavy metals. Nickel is important both as a potential pollutant and as essential microelement in the function of biocatalysts and nickel-enzymes. The focus of the paper is the influence of the chemical composition of EPS, its spatial organization, as well as the role of pH value and the hydration radius of Ni²⁺ ion in bonding process. The mechanisms of the biosorption for EPS of different composition were analyzed and proposed in relation to the structural and chemical characteristics of the system, and their interpretation is related to the Langmuir and Freundlich isotherm model. The review of the literature shows that bacterial EPS have a significant biosorption potential toward Ni²⁺ ion and that biosorption of Ni²⁺ ion with bacterial EPS is the result of several simultaneous mechanisms, where the composition and structure of EPS play a key role.

Keywords: bacterial EPS, heavy metals, nickel removal, biosorption.

INTRODUCTION

A significant environmental problem today is water pollution with heavy metals, due to their toxicity, persistence and accumulation in living organisms. Finding a solution for this problem is becoming one of the most attractive areas for researchers around the world. Due to the limitation of conventional methods for removal of heavy metal ions from aqueous solutions, biosorption has attracted increasing attention in recent years as an efficient, cost-effective and environmentally friendly approach for the water treatment [1].

Among the various biosorbents, bacterial EPS are recognized as particularly interesting biomaterials, as evidenced by the growing number of researches in this area [2]. EPS represents polysaccharide biopolymers of high molecular weight that microorganisms excrete

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into the external environment in order to survive in stressful external conditions, and they can be synthesized by both Gram-positive and Gram-negative bacteria, including non-pathogenic, pathogenic and probiotic bacterial strains [3]. The potential of EPS as a biosorbents is related to the presence of the functional groups, such as hydroxyl, carboxyl, phosphate and amino groups, which enable interaction with heavy metal ions [1,4]. Additional advantages of bacterial EPS are biocompatibility, relatively simple, environmentally friendly and economical isolation, as well as the possibility of application without chemical modification [5].

Although EPS have been studied in the biosorption of various heavy metal ions, including Pb^{2+} , Cd^{2+} , Zn^{2+} , etc., the biosorption of Ni^{2+} ions by bacterial EPS is still insufficiently researched [6]. Nickel has significant industrial importance and is frequently released into the environment, while at the same time it is an essential trace element involved in the function of certain nickel-enzymes. Therefore, the development of efficient biosorption systems for the removal of Ni^{2+} ions is of particular importance.

The aim of this review paper is to analyze and compare available research on Ni^{2+} ion biosorption using bacterial EPS, with a focus on removal efficiency (adsorption capacity), the influence of experimental conditions on biosorption, and possible mechanisms of EPS- Ni^{2+} ion interaction.

MATERIALS AND METHODS

Data used in this review paper were collected by searching scientific databases, such as Scopus, SpringerLink, Web of Science, ScienceDirect and PubMed. Relevant scientific papers and review articles related to the adsorption of nickel ions with unmodified bacterial EPS, adsorption capacities and adsorption mechanisms were analyzed. The literature search was performed by using key words related to ‘bacterial EPS’, ‘nickel adsorption’, ‘heavy metal removal’, ‘exopolysaccharides’ and ‘biosorption’. The comparative analysis includes 12 scientific papers published in period 2008-2024, while the remaining literature was used to interpret the results and discuss the mechanism.

RESULTS AND DISCUSSION

Comparative analysis of Ni^{2+} biosorption with bacterial EPS

A comparative overview of the biosorption properties of bacterial exopolysaccharides towards Ni^{2+} ions is presented in the Table 1. The table summarizes the available literature data on the biosorption of Ni^{2+} ions by chemically unmodified bacterial EPS, including EPS-producing bacterial strains and their Gram type, chemical characteristics of EPS and basic biosorption parameters. It is important to note that due to variations in experimental conditions across studies, the reported data are not directly comparable in a strict quantitative sense.

The influence of chemical composition of EPS

The differences in the values of maximum adsorption capacity (q_{max}) and efficiency of Ni^{2+} ion removal (R, %) between different EPS indicate that the chemical composition of EPS have a significant influence on their adsorption properties.

Table 1 Comparative analysis of Ni^{2+} ion biosorption with bacterial EPS

Bacterial source of EPS	Gram-type	Chemical characteristics/ functional groups	pH	q_{max} $mg\ g^{-1}$	R, %	Isotherm	Reference
<i>Alteromonas sp.</i> JL2810	G-	Uronic acids Neutral sugars Groups C=O, C-O-C, OH	5,0	344,8	n.r.	Langmuir	[7]
<i>Klebsiella oxytoca</i> J7	G-	Neutral sugars Uronic acids Aminosugars	5,5	270,0	99,3	Langmuir	[8]
<i>Lactobacillus reuteri</i> B2	G+	Neutral sugars	8,0	161,0	93,0	Langmuir	[9]
<i>Rhodococcus rhodochorus</i> 202 DSM	G+	Neutral sugars Lipids, Proteins Groups C=O, -O-C=O, C-N, amino, amide	6,5	154,1	n.r.	Freundlich	[10]
<i>Rhodococcus opacus</i> 89 UMCS	G+	Neutral sugars Lipids, Proteins Groups C=O, -O-C=O, amino, amide	6,5	129,3	n.r.	Freundlich	[10]
<i>Jeotgalicoccus huakuii</i>	G+	Groups OH, COOH, Amino, amid, phosphate	5,0	81,0	91,0	Langmuir	[11]
<i>Serratia plymuthica</i> As3- 5a	G-	Groups C=O, C=C, C-N, N-H	6,6	80,5	91,5	Freundlich	[12]
<i>Ensifer meliloti</i> MS-125	G-	Neutral sugars Uronic acids	6,0	54,0	85,0	Langmuir	[13]
<i>Agrobacterium tumefaciens</i> F2	G-	Neutral sugars Proteinaceous components Groups C=O, C-O-C	6,0	51,3	78,0	Langmuir	[14]
<i>Serratia plymuthica</i> SC3i	G-	Groups C=O, C=C, C-N, N-H	6,6	33,5	89,4	Freundlich	[12]
<i>Pseudomonas aureginosa</i> MTCC 1688	G-	Uronic acids Neutral sugars Proteins Groups C=O; amino/amide	6,0	26,7	9,0	n.r.	[15]
<i>Paenibacillus jamilae</i>	G+	Neutral sugars Uronic acids Acetic/pyruvic acids Aminosugar Proteins	5,5	17,7	n.r.	Freundlich	[16]
Mixed bacterial culture	G-	n.r.	n.r.	3,3	66,6	n.r.	[17]
<i>Pseudomonas fluorescens</i>	G-	Neutral sugars Uronic acids	n.r.	1,45	29,5	Freundlich	[18]

Table compiled and organized by the author from data reported in the literature.

Higher values of capacities and removal efficiencies were generally observed for EPS of heterogeneous composition, mainly for those with a large proportion of anionic functional groups, such as carboxyl groups. Carboxyl groups mainly originate from uronic acids, which are more commonly present in EPS with certain Gram-negative bacteria [4]. This can be linked to the specific structure of their cell wall, whose certain parts (outer membrane)

contains lipopolysaccharides that are rich in phosphates and carboxyl groups, which may contribute to the synthesis of more negatively charged EPS [3]. The Gram-type of the EPS-producing bacterium does not appear to directly determine Ni^{2+} biosorption efficiency, although Gram-negative strains more frequently produce anionic EPS.

The best adsorption capacity for Ni^{2+} ions has EPS from a Gram-negative bacterial strain *Alteromonas* JL2810, which contains a high proportion of uronic acids [7]. The chemical composition of EPS depends on the bacterial strain, its genetic potential for polysaccharide synthesis, as well as on environmental conditions that can affect the expression of biosynthetic pathways and the structures of the produced EPS.

However, anionic functional groups are not the only factor determining the efficiency of Ni^{2+} ion adsorption on EPS. This is clearly observed in EPS from Gram-positive bacterial strain *L. reuteri* B2 composed predominantly of neutral sugars, which also had a high adsorption capacity [9]. These results suggest that, besides chemical composition, the structural organization of the EPS matrix significantly influences adsorption of Ni^{2+} ions. The spatial arrangement of EPS polysaccharide chains can form 3D networks with interchain pores and microcavities that enable physical entrapment of Ni^{2+} ions within the EPS matrix [3]. Such structural organization may increase the accessibility of binding sites, in addition to the abundance of charged functional groups on the EPS surface. Additionally, such interactions can be influenced by the high hydration energy of the Ni^{2+} ions [16] and the resulting stable hydration shell which contributes to their effective hydration radius and may affect their mobility and diffusion through the EPS matrix, thereby influencing the overall adsorption efficiency.

In addition to carboxyl groups originating from uronic acids, other functional groups such as amino, amide and phosphate groups can also significantly participate in Ni^{2+} ion adsorption [1,4]. The presence of these groups increases the number and diversity of potential active sites for Ni^{2+} ion binding through electrostatic interactions, complexation, or ion exchange, thereby contributing to the overall adsorption capacity [1,16]. This is especially important for systems where the proportion of anionic functional groups is limited. Amide groups are commonly associated with protein components present in EPS matrix. Protein and lipid components may additionally increase the heterogeneity of EPS and contribute to Ni^{2+} ions binding [3], providing oxygen- and nitrogen-containing donor groups. This is, according to the table, especially pronounced in two EPS from *Rhodococcus* strains (*R. opacus* and *R. rhodochorus*), which, although they predominantly contain neutral sugars in their composition, have a high adsorption capacity for Ni^{2+} ions due to the presence of protein and/or lipid components [10]. In addition, the presence of aminosugars in the EPS structure, as in EPS from *K. oxytoca* J7 strain [8], may also contribute to the increased adsorption capacity, because they introduce additional active sites (functional groups) capable of the interaction with Ni^{2+} ions. Abundantly present hydroxyl groups in the EPS can contribute to the formation of hydrogen bonds and stabilizations of 3D polysaccharide network, which indirectly affects the availability of binding sites. Therefore, the adsorption efficiency of EPS toward Ni^{2+} ions cannot be explained solely by the presence of uronic acids, but rather to the combined contribution of multiple functional groups and the overall structural organization of the EPS.

The influence of the pH on the Ni²⁺ ion biosorption with bacterial EPS

The presented results indicate that the adsorption capacity of EPS towards Ni²⁺ ions does not depend exclusively on the pH value, but on the interaction between the environment and the chemical composition and structure of the EPS. Adsorption experiments in all the above studies were performed at pH values of 5–8. At pH values above 8, hydrolysis of Ni²⁺ ions and formation of nickel hydroxide speciation occur, which may interfere with the interpretation of adsorption result, due to possible microprecipitation and precipitation phenomena. At pH below 5, protonation of EPS functional groups, carboxyl and amino groups, is dominant, which consequently leads to a decrease in the number of negatively charged active sites for Ni²⁺ ion binding [1,3]. At the same time, the concentration of H⁺ is increased, which can lead to competition with Ni²⁺ ions for active sites on EPS.

The highest adsorption capacities were observed with EPS rich in uronic acids, or with uronic acids and aminosugars, EPSs from *Alteromonas sp.* JL2810 and *Klebsiella oxytoca* J7, which showed high efficiency of Ni²⁺ ion removal and high adsorption capacities at pH values 5,0–5,5. This can be associated with a favorable degree of deprotonation of carboxyl groups at this pH values, while the formation of hydroxide species is still limited.

EPS predominantly composed of neutral sugars (EPS from *Lactobacillus reuteri* B2) showed high adsorption capacity, which is expressed at pH 8,0 when a larger number of functional groups are in the deprotonated form. These results indicate that, in addition to the ionization of functional groups, the spatial organization of the EPS matrix is also significant, as it may increase the accessibility and exposure of active sites for Ni²⁺ ion binding and consequently enhance adsorption efficiency. In contrast, lower values of adsorption capacity were observed for EPS with a combination of neutral sugars and uronic acids at pH 6–7. These results suggest that adsorption efficiency cannot be explained solely by the ionization of carboxyl groups, since the spatial organization of EPS and accessibility of active sites within the EPS matrix may also significantly influence Ni²⁺ ion binding and adsorption efficiency.

Proposed mechanisms of Ni²⁺ ion biosorption with bacterial EPS

In Figure 1, a schematic overview of the proposed Ni²⁺ ion biosorption mechanisms in relation to EPS composition and structure is presented.

The interaction of Ni²⁺ ions with EPS mostly includes several simultaneous mechanisms, in which the dominant role is played by electrostatic interaction, ion exchange and complexation of Ni²⁺ ions with functional groups of EPS [1,16]. Carboxyl (COO⁻), phosphate (PO₄³⁻) and pyruvyl groups (CH₃COCOO⁻) contribute to the negative charge of the EPS surface and enable the binding of cations through electrostatic attraction and coordination interactions. Binding of Ni²⁺ ions to negatively charged functional groups can be also accompanied by the replacement of previously bound cations or protons from the EPS surface (ion exchange). Hydroxyl (OH⁻), carbonyl (C=O), amino (-NH₂) and amide (-CONH-) groups can also participate in metal coordination via oxygen and nitrogen donor atoms [16].

In addition to the chemical composition, the spatial organizations, porosity and crosslinking degree of EPS matrix play an important role which affect the availability of active sites for ion binding and diffusion processes. Due to the strong hydration of Ni²⁺ ion,

its mobility through the dense and less porous parts of the EPS matrix can be limited, while the structure of the polysaccharide network can contribute to ions retention in the interchain spaces.

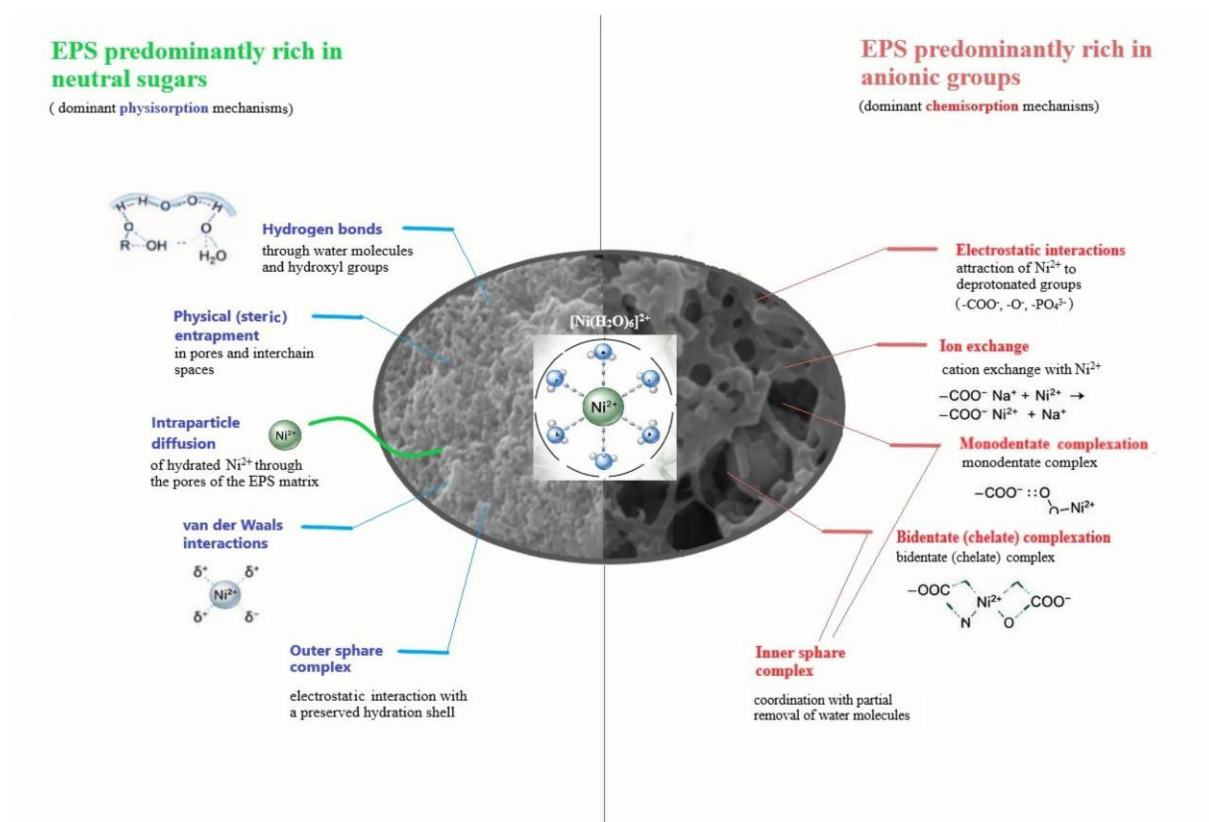


Figure 1 Proposed mechanism of Ni^{2+} ion biosorption with bacterial EPS

Although interparticle diffusion and physical trapping of Ni^{2+} ions may be more pronounced in EPS predominantly rich in neutral sugars, these mechanisms can also occur in anionic EPS, but are generally secondary in relation to binding via functional groups.

Although Langmuir's model frequently describes Ni^{2+} ion biosorption with EPS dominantly rich in neutral sugars, like from *L. reuteri* B2, the successful application of the model was also recorded in systems with more structurally complex EPS, with uronic acids, aminosugars and other components, like EPS from *K. oxytoca* J7, *Alteromonas* sp. JL2810 and *A. tumefaciens* F2. On the other hand, Freundlich's model better described biosorption with EPS which, in addition to the saccharide components, also contained other substituents such as proteinaceous and lipid components, acetyl and pyruvyl groups. This indicate that the chemical composition of EPS by itself is not sufficient for the prediction of the isothermal model, but rather the dominance and availability of certain type of binding sites and bonds that are realized with Ni^{2+} ions.

CONCLUSION

The biosorption of Ni^{2+} ions by bacterial EPS is a complex process governed by a combination of chemical composition, structural organization and environmental conditions.

Functional groups such as carboxyl, phosphate, hydroxyl, amino, carbonyl and amide groups play a central role in the binding of Ni^{2+} ions through electrostatic interactions, surface complexation and ion exchange. However, the adsorption behaviour is additionally influenced by the porosity of EPS, the degree of cross-linking, and the heterogeneity of the matrix, which determine the availability of active sites, diffusion processes and possible physical retention of hydrated Ni^{2+} ions within the EPS matrix. Differences in the composition of bacterial EPS, including the presence of proteins, lipids, uronic acids and pyruvic or acetyl substituents, contribute to differences in adsorption efficiency and agreement with isotherm models. Accordingly, the Langmuir and Freundlich models can reflect different degrees of homogeneity and heterogeneity of binding sites, while the chemical composition of EPS is not a reliable indicator of the type of adsorption behaviour. Overall, a better understanding of the relationship between the structure of bacterial EPS and the adsorption mechanisms represents an important step towards more efficient application of microbial EPS as sustainable biosorbents for the Ni^{2+} removal from water.

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