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Introductory Chapter: Biosorption

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1. Introduction

Water quality policy over the world concerning trace pollutants is defined by environmental quality standards expressed in terms of concentrations in water (Canadian Environmental Quality Standards (CEQGs); EU [1, 2]), guidelines (CEQGs; (Environment Canada [3])), ambient water quality criteria (United States Environmental Protection Agency (US EPA), n.d. [4]), and peer reviewed literature on thresholds for effects on aquatic biota (e.g., No observable effect concentrations (NOECs); lowest observable adverse effects) is a major driver of continuing interest in these measurements as part of risk/exposure (Lepom et al. [5]) as well as trend assessments (Fliedner et al. [6]).

In Europe, the adoption of the water framework directive (WFD) [7] provides a policy tool that enables sustainable protection of water resources. WFD presents a positive example of complex legislative in water quality protection.

The Decision No 2455/2001/EC of the European Parliament and the Council of November 2001 [8] established the list of 33 priority substances or group of substances, including the priority hazardous substances, presenting a significant risk to water pollution or via the aquatic environment including risks to waters used for the abstraction of drinking water.

The WFD daughter Directive 2013/39/EU [1] extended the list of priority substances to 45, including priority metal species cadmium, lead, mercury, and nickel. It also stresses the need for the development of new water and wastewater treatment technologies to address the problem of pollution by priority and river basin specific pollutants.

Nowadays, micropollutants occurring in the environment are considered to be a serious problem [9]. Aquatic environment is polluted by a broad range of these compounds from various sources including industry, agriculture, and municipal wastewaters. Many of those compounds are present at low concentrations in the environment, but they still pose and

toxic effects to aquatic organisms, and human health. Their efficient removal from water and reduction of risk presents a new challenge for water managers and development of new water treatment technologies present a challenge for the scientific community [10].

The most problematic micropollutants in waters are heavy metals, pesticides, industrial chemicals and byproducts, personal care products, pharmaceuticals, and other substances that can be toxic to wild animals and humans at low concentrations. Currently, available wastewater treatment technologies are often expensive or ineffective [11]. Research results confirm that large amounts of conventional waste, including egg shells, bones, peat, mushroom, seaweed, yeasts, and carrots [12, 13] show the ability to effectively remove heavy metals from pickled water.

Biosorption refers to a set of processes that involve physical and chemical adsorption, ion exchange, electrostatic interactions, complexation, chelation, and microprecipitation, that occur in the cell wall and precede the anaerobic or aerobic biodegradation processes. It is characterized by high selectivity and efficiency (high performance and low cost). Natural materials, such as marine algae or weeds, or industrial waste, such as excess activated sludge or fermentation wastes, may be used as biosorbents.

Biological sludge wastewater treatment processes utilize biosorption and bioaccumulation as part of organic and inorganic pollutants, priority substances, heavy metals, and organic pollutants/micropollutants removal mechanisms.

The idea of using biomass in technologies to protect the environment originates at the early twentieth century when Arden and Lockett found that some species of living bacteria are capable of removing nitrogen and phosphorus from wastewater during aeration [14–16]. This process is known as activated sludge process. The removal mechanism has been explained in the context of bioaccumulation capacity. This phenomenon as well as the activation process itself has continued to be widely used. The break occurred in the late 1970s of the last century. Knowing the sequestration nature of biologically inactive biomass has led to a shift in research from bioaccumulation to biosorption [17].

The interest in biosorption of organic and inorganic pollutants stems from the fact that these substances are toxic and can destabilize the food chain [18]. The absorption of substances by microbial biomass is generally referred to as biosorption. The mechanism responsible for this accumulation is complex and includes, among other processes, adsorption to the cell surface and/or absorption of the substances into various compartments of the microbial cell. Microbial cells have a disposition to concentrate chemicals from the aquatic environment. Therefore, it is necessary and important to understand the mechanisms and kinetics of biosorption, bioaccumulation and biodegradation processes, and their interactions that govern the fate of hazardous inorganic and organic pollutants in biological treatment of wastewater.

2. Mechanisms and kinetics of biosorption

2.1. Biosorption and bioaccumulation

Biosorption is a physicochemical process that utilizes the mechanisms of absorption, adsorption, ion exchange, surface complexing, and precipitation processes. It is a spontaneous process

independent of the metabolism of microorganisms. In biotechnology, it is used to separate inorganic and organic substances from the solution using biosorbents. Biosorption is an important process also in protecting the environment.

Biosorption is defined as the passive adsorption of toxic substances by dead, inactive or biologically derived materials. Biosorption is a consequence of several metabolic processes independent of the cell membrane, the mechanisms responsible for the absorption of the pollutant vary according to the type of applied biomass.

Bioaccumulation is defined as the phenomenon occurring in living organisms. More specifically, bioaccumulation is defined as the absorption of toxic contaminants by living cells or organisms. Compounds are passively or actively transported into cells, accumulated inside them, and they also enter the metabolic cycle through the cell membranes. Bioaccumulation is therefore often dependent on cell metabolisms.

Both bioaccumulation and biosorption have certain advantages and disadvantages. In general, the use of living organisms is not suitable for continuous water purification processes from highly toxic organic/inorganic contaminants. If the concentration of the toxic substance is too high or the process step takes a long-time period, the accumulated substance quantity may reach partition equilibrium, or saturation. Due to the high accumulated pollutant concentration the metabolism of the organism will be disturbed and death may occur. This scenario can be avoided by using inactive, dead biomass. Moreover, if the sorption process is reversible, compounds may be desorbed back to the treated water if the concentration drops. To avoid desorption, a high sorption capacity has to be provided. This is not always feasible in processes applying living cells, because of various restrictions such as requirements of nutrients, aeration, maximum cell density, and so on. This is why we devote more attention to biosorption than bioaccumulation.

2.2. Mechanisms of biosorption

Biosorption of heavy metals and organic compounds occur due to the physicochemical interactions between the metal and the functional groups present at the surface of the biosorbent. The processes involved include physical adsorption, ion exchange, and chemical sorption that are not related to metabolism. The cell walls of microorganisms consist mainly of polysaccharides, proteins and lipids and have carboxyl, sulfate, phosphate and amino groups to form bonds with metals, and their complexes. Such biosorption occurs relatively rapidly and can be reversible [19]. Various mechanisms of removal of heavy-metal by activated sludge microorganisms are discussed in more details e.g. by Pagnanelli et al. [20].

Organic pollutants differ significantly in their structure. As a result, biosorption is affected by molecule size, charge, solubility, hydrophobicity, and reactivity. The biosorbent process can also significantly influence the type of biosorbent and the composition of wastewater [21].

The lipophilic nature of the hydrophobic compounds allows them to pass through cell membranes and absorb into the organic cell matrix. An important component of biosorption of organic pollutants may be absorption in cell membranes or lipid containing cell structures. Other mechanisms are involved in biosorption include surface adsorption, chemisorption,

and complexation [22]. For more detailed information we refer the reader to the work Fomina and Gadd [21].

2.3. Modeling of biosorption

The equilibrium distribution of the sorbed pollutant (sorbate) between the sorbent and the aqueous phase is required to determine the maximum sorbent's uptake capacity for a sorbate and to understand the sorption mechanism.

Besides sorbate distribution at equilibrium, the sorption kinetics provides additional important information about the sorption mechanism, especially the rate of pollutant removal. When applied in water treatment technology, information on sorption kinetics is important for setting an optimum residence time of the wastewater at the biosolid phase interface.

2.3.1. Adsorption isotherms

To describe the concentration-dependent equilibrium between the pollutant amount adsorbed on the cells (a) and the pollutant concentration dissolved in aqueous solution (C_e) at equilibrium conditions and constant temperature, which is referred to as the adsorption isotherm. Langmuir, Freundlich, Langmuir-Freundlich, Redlich-Peterson, Brunauer-Emmett-Teller (BET), and Radke-Prausnitz models are the most frequently cited literature in the literature [23–26].

When sorption equilibrium is reached, the adsorption capacity can be calculated from mass balance in a batch sorption system consisting of a discrete volume of water and adsorbent:

$$a \ = \ \frac{V}{m}(C_0 - C_e)$$ (1)

where a is the sorption capacity (kg.kg^{-1}), V is the volume of water/wastewater (m^3) treated in a single sorption step, m is the mass of the adsorbent (kg), C_0 and C_e are the initial and equilibrium aqueous adsorbate concentration (kg.m^{-3}), respectively.

Most often, pollutant distribution is concentration-dependent and in such case non-linear forms of adsorption isotherms are used to describe experimental data resulted from batch adsorption measurements. Langmuir isotherm is defined assuming that adsorption takes place at specific homogeneous sites at the surface of the adsorbent. This means that once the molecule of the adsorbed substance occupies a sorption site, no further adsorption can occur at this site. The Langmuir adsorption isotherm [23] has the form:

$$a \ = \ \frac{a_{max} \ . \ b \ . \ C_e}{1 + b \ . \ C_e}$$ (2)

Where a_{max} (kg.kg^{-1}) is the maximum biosorbent capacity of the adsorbent in the formation of a saturated monomolecular adsorption layer and b (L.kg^{-1}) is Langmuir's empirical constant associated with the free energy of biosorption.

Freundlich's isotherm [24] was postulated for adsorption at heterogeneous surfaces and it takes the form:

$$a = k \cdot C^{1/n} \tag{3}$$

where k (L.kg^{-1}) is a Freundlich constant referring to biosorbent capacity and n (dimensionless) is a Freundlich constant indicating the intensity of biosorption. Freundlich isotherm does not take into account the saturation of biosorbents.

Tempkin isotherm [25] assumes that biosorption energy decreases linearly with increasing saturation of biosorption sites, rather than decreasing exponentially, as Freundlich isotherma suggests. Tempkin isotherm is given as follows:

$$a = \frac{R \cdot T}{b_{Te}} \cdot ln\left(a_{Te} \cdot C_e\right) \tag{4}$$

where a_{Te} is the Tempkin isotherm constant, b_{Te} is the Tempkin constant referring to the biosorption energy, R is the universal gas constant (8.314 J.mo^{l-1}.K^{-1}), T is the thermodynamic temperature (K), and C_e is the equilibrium pollutant concentration in solution.

BET (Brunauer, Emmett, and Teller) isotherm is described by the following equation [26]:

$$a = \frac{a_{max} \cdot d \cdot C}{(C_e - C) \cdot \left(1 + (d-1) \cdot C/C_e\right)} \tag{5}$$

where C_e is the equilibrium concentration of adsorbate (kg.m^{-3}), d is the constant expressing the energy of sorbate interaction with the sorbent surface.

2.3.2. Kinetics of adsorption

A pseudo-first order model [27] and the pseudo-second order kinetic model [28] can be applied to fit the experimental data and evaluate the adsorption kinetics.

The Lagergren pseudo-first order model suggests that the rate of sorption is proportional to the number of sites unoccupied by the solutes. The pseudo-first order model can be written in linearized form as follows:

$$a_t = a_e\left(1 - exp\left(-k_1 \cdot t\right)\right) \tag{6}$$

where a_e is the amount of pollutant biosorbed at equilibrium (mg.g^{-1}), a_t is the amount of pollutant biosorbed (mg.g^{-1}) at any time t, and k_1 is the first order rate constant (min^{-1}).

The pseudo-second order kinetic model can be written in linearized form as follows:

$$a_t = a_e\left(\left(1 - \frac{1}{1 + a_e \cdot k_1 \cdot t}\right)\right) \tag{7}$$

where k_2 is the second order rate constant (g.mg^{-1}.min^{-1}).

The pseudo-second order model does not identify the diffusion mechanism.

From the majority of biosorption-related work, it follows that the pseudo-first order equation does not describe well-meaning values throughout the contact time. Generally, this equation is only applicable in the initial phase of the adsorption process. This is due to the fact that, using the linearized form of Eq. (6) it is necessary to know the value of the equilibrium adsorption capacity, which can be approximated by the extrapolation of experimental data for infinite time, i.e., the trial and error method. On the other hand, it is not necessary to know this value for the use of the linearized form of the kinetic equation of the pseudo-second-order.

In this context, it should be emphasized that using a non-linear method of determining the values of parameters of non-linear equations in general it is possible to avoid such errors in the modeling of process kinetics.

3. Biosorbents

For several decades, biosorption has been referred to as perspective, low-cost biotechnology applicable in wastewater treatment. However, despite intensive research, significant advances in the knowledge of these complex processes and rich magazines and book publications, the practical application of this process and related technologies are not adequate so far [20].

Previous research has focused on testing the development of more suitable and available biological materials. The biosorbent materials used may be alive or deactivated microorganisms and their components, plant materials, industrial and agricultural wastes, and natural processing residues, e.g. wood, wood bark, and sea algae.

Both live and dead biomass can be used to remove hazardous substances. The inactive (sterilized, dried, and/or otherwise chemically treated) biomass benefits from no need of supplies of substrate, nutrients, eventually oxygen, which would otherwise be needed in order to maintain viable biomass during adsorption. Also, the toxicity of pollutants to be removed by biosorption poses no problem.

Biosorbents for the removal of toxic metals or organic pollutants mainly use biomass of bacteria, yeasts, fibrous fungi, algae, as well as wastes from food and pharmaceutical production, agricultural waste, and other polysaccharide materials. All biomaterials should demonstrate good biosorption capacity and affinity for all types of inorganic ions and organic compounds.

Important biosorbents of the fungus family include the filamentous fungi of the genus *Alternaria, Aspergillus, Rhizopus, Penicillium,* and the yeast *Saccharomyces cerevisiae* and *Saccharomyces carlsbergensis*. These microorganisms are widely used in the food and pharmaceutical industry and end up as waste that is available from individual free or low-cost production. Another important biosorbent to which attention is focused are marine algae, which are also biological resources. The algae include red, green and brown algae, with brown algae being among the excellent biosorbents, for example, *Chlorella vulgaris*.

This is due to the alginate content that is present in the form of gel in the cell walls. The macroscopic structure of the algae provides a conventional basis for the production of biosorbents suitable for the application of sorption processes. It should be noted that algae are not considered

waste; in fact, they are the source for the production of agar, alginate and, carrageenan. This means that the choice of algae for biosorption purposes needs to be given the utmost attention.

Scientists work mainly with brown algae using one of the best metal sorbents seaweed, Sargassum seaweed. They focus on the study of sorption properties and biosorption mechanisms. Biosorbents using algae, bacteria, fibrous fungi, and yeasts are also used for analytical techniques, specifically for solid phase extraction to determine metals present in trace amounts in different aqueous matrices [29].

Microbial biomass (bacteria, fungi, and micorrhagia) shows better results of biosorption of dyes than macroscopic materials (seaweed, squirrel crabs, etc.). The reason is the difference in cell wall and functional groups involved in dye binding. Many bacteria, fungi, and microorganisms bind different types of dyes.

The results of the study by Simionato et al. [9] show that the use of chitosan obtained from silkworm chrysalis is a viable alternative for the removal of blue remazol and black remazol five dyes from the wastewater of the textile industry. Potential biosorbents belonging to the class of bacteria include *Bacillus*, *Geobacillus*, *Lactobacillus*, *Pseudomonas*, *Streptomyces*, *Staphylococcus*, *Streptococcus*, and others.

Several studies have recently been carried out to develop cheap sorbents from industrial and agricultural waste. Partial attention was paid in particular to crab shells, activated sludge, rice husks, egg shells, mosses, and lichens. The results showed that, in particular, crab shells have excellent sorption abilities in relation to arsenic, chromium, cobalt, and nickel.

A preferred biosorbent material is activated sludge. There are a large number of binding sites on the cell walls of microorganisms, which are predominantly composed of polysaccharides, proteins, and lipids. This is due to the high biosorption capacity of activated sludge. The amount of excess sludge produced mostly outweighs the possibilities of its use and represents one related problem of wastewater treatment. Thus, this biosorbent is reely available and low-cost.

Authors [30–32] disclose the advantages of using aerobic and anaerobic deactivated sludge to remove dyestuffs and hazardous effluent from wastewater. Qiu et al. [33] presented the results of research into the use of active aerobic and anaerobic sludge for sewage treatment.

The extent of biosorption depends on the type of biomass [34]. In the past, biosorbent phenomena have often been found to bioaccumulate highly hydrophobic organic substances directly depending on the lipid content of biomass. However, non-polar substances have been found to accumulate in organisms according to the distribution equilibrium between the medium and the lipid content of the organism [35]. Other authors found the opposite phenomenon to track DDT [Dichloro-Diphenyl-Trichloroethane or 1,1,1-Trichloro-2,2-bis(p-chlorophenyl)-ethane] adsorption by different soil fractions [36]. Some soil fractions were first extracted with ether and ethanol to remove lipid-like substances. Absence of lipid-like materials did not decrease, on the contrary, increased DDT adsorption with soil, indicating that other substances other than lipids may also play a role in biosorption. A similar finding was obtained by monitoring the adsorption of chlorites with microbial biomass [37]. Bacterial biomass with the highest lipid content among the observed samples had the lowest biosorption capacity. Further, it has been found that in different samples of fibrous fungi biomass, despite the similar lipid content in the

cells, the biosorption capacity varied within a wide range. Interestingly, however, it was found that the biosorption capacity of different biomass samples depended directly on the amount of total organic carbon released during the contact of biomass with the pollutant. However, this phenomenon is not elucidated, it can only be assumed that the biosorption capacity increases with the growing proportion of cells destroyed in the medium, which correlates with the total organic carbon content released into the medium. Cell fragments have a larger surface and thus a higher sorption capacity [38]. The authors further found that the biosorption capacity of active and deactivated (inactive/dead) biomass is almost the same for highly biodegradable pollutants.

4. Research and applications of biosorption

4.1. Removal of organic pollutants

Biosorption acquires meaning for the removal of hazardous substances. It can be used as an individual separation process or may be a part of others, biological processes. Aksu, in the review paper [39], deals with the application of biosorption to remove organic pollutants. Among the studied pollutants are pesticides, phenols that are toxic and persistent in the environment.

Various types of pesticides are used in agriculture. Some of them are persistent, have mutagenic and carcinogenic effects, and are generally toxic. Suitable sorbent for removing them appears to be activated carbon. Its disadvantage is the high price. Regeneration of granular activated carbon is also costly.

This has motivated researchers to explore the possibility of using alternative materials that originate in nature or are the waste of other processes, peat, soil, wood, eucalyptus bark, rice husk, chitin, fly ash, or surplus activated sludge. These are relatively inexpensive materials but are usually characterized by low adsorption power values. This disadvantage can be compensated by larger amounts of adsorbent [40, 41]. An alternative for the recovery and/or environmentally acceptable disposal of pollutants could be, passive adsorption of pollutants from aqueous solutions using a renewable non-living microbial mass. The specific surface properties of bacteria, fungi, yeasts, and algae allow the adsorption of various types of pollutants from solutions. More advantageous is the use of inactivated microorganisms. They are not dependent on creating conditions for maintaining metabolic function, including eliminating the effects of toxic substances. They can be stored for a longer period, easily regenerated and reused [39].

The biosorption mechanism on inertial biomass is influenced by the biomass itself, the properties of its surface characteristics, the physical and chemical properties of the adsorbed substances, their mutual affinities, and experimental conditions (pH, temperature, ionic strength, existence of competing organic substances or inorganic ligands in solution).

Conversely, due to the fact that hydrophobic organic pollutants show a high tendency to accumulate on microbial cells or sludge, living biomass can be used to remove very low concentrations of hazardous organic substances from wastewater [42, 43].

Most dyes are of synthetic origin. They are characterized by an aromatic structure, greater stability, and a worse biodegradability. They can affect the processes of photosynthesis in the aquatic environment to toxicise the aquatic ecosystem [44, 45]. Research results [44–46] show that there is a wide range of microorganisms, including bacteria, fungi, and algae, which are capable of biodegradation or bioaccumulation of azo dyestuffs in wastewater by anaerobic/ aerobic processes.

For the modeling and optimization of processes using sorption on the activated sludge, the necessary is knowledge about the sorption of organic matter to the sludge. Modin et al. [47] compares primary, anaerobic, and aerobically activated sludge as biosorbent materials. Bio-sorptive capacity values were determined, process kinetics was studied, and some characteristics of sorbed organic matter were studied. Biosorption of dissolved organic substances occurred almost immediately. This was followed by a slower process that corresponded to first-order kinetics. Biosorption of undissolved particles also corresponded to first order kinetics. However, there was no immediate sorption, but the particles were released during mixing.

Biosorption is used for wastewater treatment since the beginning of the last century, when the activation process was discovered. Controlled withdrawal of excess sludge together with significant participation of biosorption a bioaccumulation processes enable intensification of organic pollutants, nitrogen, and phosphorus removal. Bioaccumulation is usually an active process that is part of the metabolism of microorganisms. Biosorption is a passive process of adsorbing pollutants on the surface of microorganism cell walls. This leads to a decrease in the concentration of these substances in the purified water. However, such contamination remains a part of the activated sludge and its re-release to the environment is dependent on further treatment with the excess sludge produced, especially if the biosorption of these substances is reversible.

An increasingly serious challenge is dangerous (organic) and so-called emerging pollutants, e.g. pesticides, estrogens, personal care products, or pharmaceuticals. These can be removed in the wastewater treatment plant by biotic and abiotic processes, or they can pass through the sewage treatment plant to the recipients without any significant change. In the context of minimizing the production of excess sludge, its disintegration prior to the process of biological stabilization and degradation of biosorbable pollutants on activated sludge, the combined processes of biosorption and chemical oxidation, e.g. using ozone.

The solubility of the pollutant is an important property affecting biosorption. The inverse relationship between water solubility and accumulation of organic molecules with biomass was found [9]. In general, the different types of biomass observed had a greater biosorption capacity for less soluble pollutants. Organic molecules accumulate better in microbial bio-mass, the higher the biomass-water distribution coefficient (octanol-water model system), but as already mentioned above, there is no direct correlation between biosorbent capacity and lipid content in biomass.

If the contaminant dissociates in the aqueous phase (on a weak acid or a weak base), sorption of the dissociated and non-dissociated forms can take place with different sorption coefficient values for both forms [15]. The effect of the initial concentration of the pollutant on the rate of biosorption was monitored. After 10-fold increase in the initial concentration of the pollutants

studied (lindane pesticides and diazinone), the rates of biosorption of these substances on activated sludge were higher for higher concentrations of pollutants.

It can be assumed that in a system containing a mixture of several pollutants of a similar nature, the biosorption capacity of the individual components of the mixture will be affected by the concentration of the other substances in the mixture. A reduction in biosorbent capacity of tetrachloroethane on the *Rhizopus arrhizus* biomass has been shown to be up to 14% in the presence of the same concentration of trichloroethane [13]. Biosorption is usually an exothermic process, so biosorption capacity usually increases with decreasing temperature. However, the change in temperature does not significantly affect the rate of biosorption [8].

Simjonato et al. [9] studied the process of adsorption of blue remazol and black remazol five dyes with chitin and chitosan, which they performed in the column and an aqueous suspension. The results show that better results were obtained in the column with arthritis than in the chitin-packed column. Comparing the results measured in the column and suspension results in better suspension results. A very good description of Langmuir isothermal experimental values was obtained, with the difference between the measured and calculated adsorption capacity values being insignificant.

Biosorption of hazardous pollutants is a suitable technology for removing dyestuffs from municipal and industrial wastewater. Various low-cost biosorbents, such as, for example, biomass of algae, yeast, fungi, vegetable waste, fiber, fruit waste, chitosan, and agricultural waste were studied [48].

4.2. Removal of heavy metals

Biosorption and bioaccumulation can also be applied to remedy environments contaminated with heavy metals as complementary methods to currently used physical and chemical methods. It was found that removal of heavy metals from the environment with biotechnological methods should consider a number of physicochemical factors such as temperature, pH, contact time of biomass, and a solution containing metals, concentration and age of biomass, and toxicity when living microorganisms are applied. Improving the efficiency of removal of metals can be performed through physical and chemical modifications and immobilization of biomass. The most frequently applied reactors include stirred tank reactors, fixed-bed, reactors and fluidized-bed reactors [49].

In the process of biosorption, ions of metals are adsorbed on the surface of a sorbent. Biosorption is a metabolically passive process that uses dead biomass. Biosorption is the first step of bioaccumulation [49].

Environmental pollution of heavy metals is one of the most serious environmental problems. Various biosorbents such as fungi, yeast, bacteria, and algae are used to remove them. These biomaterials are considered to be cost-effective for high-volume and low-heavy wastewater treatment (from 1 to 100 mgl^{-1}). The promising biomaterials for heavy metal removal include *Saccharomyces cerevisiae* fungus. This fungus is commonly used in food and beverage production. Low-cost media is sufficient to cultivate it. It is a by-product/waste from the fermentation industry.

Mustapha and Halimoon [19] examined the microorganisms and mechanisms of heavy metal biosorption in the environment.

Bacterial biosorption is mainly used to remove pollutants from wastewater contaminated by pollutants that are no1t biodegradable, such as metal ions and dyes [19]. Rats are efficient and inexpensive biosorbents, because the requirement for algal nutrition is low. Based on a statistical analysis of algae potential in biosorption, algae were reported to absorb about 15.3–84.6%, which is higher than other microbial biosorbents. All types of brown algae were known to have a high absorption capacity. The metal ion biosorption occurs on the cell surface using the ion exchange method. Brown marine algae have the ability to absorb metals through chemical moieties on their surface such as carboxyl, sulfone, amino, as well as sulfhydryl [19].

The use of fungi as a biological sorbent has been shown to be an effective material, and is also one of the cost-effective and environmentally friendly methods that serve as an alternative to the chemically bonded processing process. The ability of many types of fungi to produce extracellular enzymes to assimilate complex carbohydrates for previous hydrolysis causes the degradation of various degrees of pollutants. Compared to yeast, fibrous fungi are less sensitive to nutrient sweeps, aeration, pH, temperature, and have a lower content of nuclei in biomass [50, 51].

Microbial biomass is one of the cheap and effective biosorbents for removing heavy metals from solutions. The biosorption process has many attractive properties including the removal of metal ions in a relatively wide range of pH and temperature. Many researchers have studied the biosorbent performance of various microbial biosorbents that provide good arguments for introducing biosorption technologies for removing heavy metals from solutions, as well as understanding the mechanism responsible for biosorption [19].

4.3. Removal of micropollutants

The large occurrence and presence of micropollutants (MPs) in the aquatic environment is one of the major challenges worldwide. For example, in 2012, some 143,000 compounds were registered on the European market, many of which at some point in their life cycle would end up in the aquatic environment. Most of them are not removed or transformed into conventional wastewater treatment plants (WWTPs), they can persist in the aquatic environment or create new chemicals by reaction with humic substances and sunlight, and they can be bioactive and can bioaccumulate [52–56].

Although present in almost undetectable (ppb; part per bilion) concentrations, their presence in the aquatic environment is associated with various deleterious effects in organisms such as estrogenicity, mutagenicity, and genotoxicity [57].

There is no legal regulation for removing MPs in WWTPs. However, there are some (EU) regulations that set limit values for certain substances that have specific MP properties, pesticides, lindane, nonylphenol, and synthetic hormones [58] in water.

MP can be divided into several categories such as pharmaceuticals personal care products (PPCP), household chemicals and industrial chemicals. A comprehensive list of 242 chemicals

is included in the EU 7PP [59] project of which approximately 70% are pharmaceutical and personal care products, and 30% are industrial products, including perfluorinated compounds, pesticides, herbicides, and food additives.

The vast majority of MP in municipal wastewater belongs to the class of personal hygiene drugs and products PPCP, the fate and processes for removing these compounds are discussed in detail in this text.

About 70% of the wastewater products come from the household, 20% come from livestock, 5% come from hospital wastewater, and the remaining 5% come from outflows from non-specified sources [60].

The removal of micropollutants in wastewater treatment plant depends on their solubility, octanol/water partition coefficient, and Henry's constant. For removing micropollutants in wastewater treatment plants significantly contributes their sorption on suspended particles of primary and secondary sludge. Removal of dissolved organic compounds also involves coagulation, flocculation and biodegradation processes. The majority of conventional wastewater treatment plants do not completely remove these substances. Their removal is influenced significantly by the operational conditions, the biochemical environment (aerobic, anaerobic, anoxic, sludge age (SRT), temperature, pH, and redox potential.

4.4. Biosorption in municipal wastewater treatment

Biosorption and bioaccumulation mechanisms continue to play an important role in newly developed processes and technologies for wastewater treatment.

The fate of the priority substances and micropollutants that are transported by wastewater to wastewater treatment plants (WWTPs) depends on their adsorption on suspended particulates, dissolved humic substances, primary and secondary sludge. Adsorption of insoluble matter in primary and secondary treatment units is an important process of MP removal from wastewater. Adsorption may occur as a result of hydrophobic interactions between aliphatic and aromatic groups of lipid fractions in the primary sludge and the lipophilic cell membrane of the microorganisms in secondary sludge. Interactions also occur between positively charged MP groups and negatively charged microorganisms in secondary sludge.

4.4.1. Integrated and hybrid processes

Both the development of the activated sludge process and the increasing wastewater pollution are also developing biosorption applications. It is, for example, hybrid activated sludge process with activated carbon. Interaction of bio-degradation and adsorption on activated carbon benefits from the higher efficiency and performance of the process due to the concentration of organic matter on activated carbon, consequently higher rates of biological oxidation, as well as better conditions for the degradation of resistant substances, especially for industrial wastewater treatment and groundwater remediation.

In the 1950s of the last century, the activated sludge process with separate sludge regeneration was put into full-scale operation, where the ability to accumulate a substrate was restored. In addition

to reducing the volume of aeration tank required and reducing investment costs, this bioreactor configuration is characterized by a high resistance to filamentous sludge bulking. The above mechanisms are also used as part of enhanced biological phosphorus removal processes [14–16].

In a hybrid system, slow and fast biodegradable substances and simultaneous macronutrient removal processes can be carried out by combined activated sludge and immobilized biomass [61]. Higher biomass concentrations and two different solid retention times significantly influence biosorption/bioaccumulation processes and ultimately, their participation in the whole complex of the biological wastewater treatment.

Biosorption and biodegradation also increase the efficiency of anaerobic sludge stabilization. Current research is mainly focused on increasing the efficiency of sludge stabilization. It is also focused on the research of anaerobic decomposition of micro-pollutants. However, there is little information and knowledge about biosorption potential and biosorption mechanisms of these substances. Information on pollutant biosorption on anaerobic sludge is important not only for the removal of pollutants themselves but also for the modeling of biological sludge stabilization systems [33].

Accumulation of dangerous hydrophobic organic pollutants, e.g. in activated sludge biosorption results in their removal from the wastewater stream, but the resulting disposal of contaminated sludge then poses a new environmental problem, especially when pollutants are bound to microbial sludge reversibly [33]. Reduction of sludge mass during stabilization leads to concentration of accumulated compounds, but potentially also to increase of their chemical activity as a result of reduction of sludge sorption capacity in the stabilization processes. This may lead to an increased risk related to compounds sorbed to the stabilized sludge.

However, such contamination remains a part of the activated sludge. Its release to the environment is dependent on further treatment with the excess sludge produced, especially if the biosorption of these substances is reversible.

One of the current trends in the sludge management and the minimization of the release of priority substances and micro-nutrients through the application of the sludge in agriculture is the research of integrated biological and chemical processes to minimize the production of excess sludge and carry out the simultaneous transformation/degradation of micropollutants sorbed on activated sludge [62–63].

5. Conclusions

The past decades brought intensive research leading to an understanding of biosorption processes with the aim of their application in water treatment technology t. Numerous papers were published that significantly contributed to a better characterization of complex phenomena involved in biosorption. Information was gathered on the bioprocess mechanisms and the influence of various factors in the removal of inorganic and organic pollutants by biosorption.

In spite of targeted research on alternative low-cost sorption materials and extensive knowledge and publication results, it was not possible to apply this process practice in great extent, so far.

Further research into the practical use of biosorption to remove specific organic and inorganic pollutants will obviously be geared toward increasing the overall efficiency of the process, not only in terms of cost but also its performance.

The importance of sorption and biosorption processes in wastewater treatment processes and technologies, aerobic and anaerobic sludge stabilization is increasing. New development trends include integrated and hybrid processes aimed at minimizing sludge production and preventing the release of priority substances and micropollutants into the environment through the application of sludge to the soil.

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