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EFFICIENCY OF WATER POLLUTION TREATMENT BY VARIOUS ADSORPTION METHODS – A REVIEW

EFIKASNOST TRETMANA ZAGAĐENJA VODE RAZLIČITIM ADSORPCIONIM METODAMA - PREGLED

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Abstract: Pollution of the environment, especially the water as one of the integral ecosystem's constituents, is a problem of high significance, escalating on a global level. Watercourses are often contaminated by heavy metals, originating from various anthropogenic sources. This study aimed to give a survey on studies conducted on wastewater treatment technologies based on the adsorption mechanism using diverse sorbent types, such as inorganic composite materials, plant biomass, and nanomaterials. Further researches, development of new technologies, and optimization of the existing ones are required for the successful overcoming of the water contamination problem and their wide application in practice.
Key words: adsorption, heavy metals, inorganic composites, biomass, nanomaterials

Rezime: Zagađenje životne sredine, posebno vode, kao jednog od sastavnih sastojaka ekosistema, problem je od velikog značaja koji eskalira na globalnom nivou. Vodotoci su često zagađeni teškim metalima, koji potiču iz različitih antropogenih izvora. Ova studija je imala za cilj da pruži pregled studija sprovedenih o tehnologijama prečišćavanja otpadnih voda zasnovanih na adsorpcionom mehanizmu koristeći različite tipove sorbenata, kao što su neorganski kompozitni materijali, biljna biomasa i nanomaterijali. Dalja istraživanja, razvoj novih tehnologija i optimizacija postojećih neophodni su za uspešno prevazilaženje problema zagađenja voda i njihovu široku primenu u praksi.
Ključne reči: adsorpcija, teški metali, neorganski kompoziti, biomasa, nanomaterijali

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1. Introduction

As technology development continues, heavy metals in surface and ground waters continue to exceed guideline controls established by WHO and other regulatory organs [1]. Due to their complicated degradation, environmental stability, facile accu-mulation, and predisposition to be transformed to more toxic organic forms, the risk associated with heavy metals has drawn escalating attention [2]. Some heavy metals possess bioimportance as trace elements, while there are more of them with no beneficial effect, such as Pb, Cd, Hg, and As, whose proved biotoxicity causes a series of adverse effects to the metabolism of humans and other biota [3]. Environmental concerns of the water contamination expansion as a health risk threatening the entire biosphere led to global seeking for a sustainable, reliable, and affordable technology universally applicable for different pollutants. Meeting all requirements for successful water remediation obstacles overcoming remains a challenge, due to the matrix complexity and contaminants variety [4]. Some of the main drawbacks are the generation of hazardous byproducts, low removal and non-cost-and-energy efficiency, and the inclusion of more toxic chemicals into the environment [5]. Among numerous water decontamination techniques, EPA (US Environmental Protection Agency) declared adsorption as the best available technique (BAT) - the most productive, effortless, environmentally friendly, and economical wastewater purification method [5]. It is suitable for soluble and insoluble organic, inorganic, and biological contaminants and is applicable both for potable and industrial water [6]. A large variety of adsorbents, such as activated carbon, metal oxides, resins, biomaterials, clays, zeolites, and nanomaterials, have been developed and examined for their capability to eliminate various types of pollutants from waters. This review aimed to evaluate the current state of adsorption techniques utilization based on inorganic composites, biomass, and nanomaterials, its main advantages and existing challenges regarding these adsor-bents, as well as potential upcoming perspectives.

2. Heavy metals and health risk

Contaminated drinking water represents the primary source of human exposure to toxic metals. Cations of these metals may bind with various functional groups in biomolecules, creating stable complexes and damaging their activity and structure [7]. Because of the matching ionic radius, heavy metals could replace essential elements in biomolecules leading to the loss of biological activity and cellular functions disrupting. Geometry, structure, and charge distribution of the formed complexes could be similar to amino acids, hormones, and neurotransmitters so they can communicate with the corresponding receptors, while long-term exposure may lead to harmful consequences to nervous, immune, and endocrine systems [8].

3. Adsorption mechanism

Adsorption represents a mass transfer process from the aqueous phase onto the solid phase surface and binding by physicochemical interactions. Adsorbate migration occurs in the following steps: 1) adsorbate migration to the adsorbent border, 2) diffusion into adsorbent pores, 3) adsorption and desorption of solute [4]. These steps are governed mainly by 1) the characteristics of the matrix (solution), such as pH, temperature, pressure, ionic strength, the presence of the background and competitive solutes, 2) adsorbate properties – geometry, size, hydrophobicity, dipole moment, molecular weight, polarity, and solubility, so as 3) the adsorbent features including pore size and volume, surface area and charge. The assessment of the maximum adsorption capacity of the material utilizes adsorption isotherms.

4. Adsorbents

The selection of a suitable adsorbent relies on knowledge about the type of pollutant and its concentration in the water, adsorbent efficiency, and the adsorption capacity for the present contaminant(s) [5]. Non-toxicity, cost-effectiveness, easy availability and regeneration, are some of the demands potential adsorbents should fulfill. Many operational parameters affect adsorbents' efficiency for heavy metal removal, such as temperature, pH, adsorbent dosage, initial concentration, stirring speed, and contact time [9]. Certain promising adsorbents with high potential for enhancements and large-scale application development are described below.

4.1. Inorganic composites

Composite materials have reached significant popularity in numerous spheres. Considerable attention by the research community has been devoted to combining metal oxides, principally binary ones, to create composite sorbents possessing desired properties for water pollutants removal. Combined elements have an affinity for contaminants or chemical and mechanical resistance, while the final amalgamated material retains the initial features of all constituents. Good mechanical properties, such as strength, adsorbent particles and resistance to destruction, and chemical characteristics of the sorbent – surface ionization degree, functional groups types, and variations in sorbent response due to the contact with the solution, are of great importance in determining of sorbent adsorption capacity. Combinations of Fe-Mn were found sui-table for cobalt removal, Al-Si, and Fe-Mn for selenium elimination, and Zr-Mn and Sn-Mn for mercury removal [10].

Due to their high adsorption performance, easy generation and modification, and low cost, the development of hybrid adsorbents, by La3+, Ce4+, and Zr4+, MnO2 incorporation into the TiO2 attracted much interest in past years [11]. Oxides of the rare earth elements, such as synthesized Zr-TiO2 compo-site obtained using the microwave hydrothermal method, demonstrated effective water purification from As3+ and As5+ [11]. Binary oxide Fe-Mn (FMBO) adsorbent also could simultaneously remove As3+ and As5+, so as Sb3+, where manganese oxide enables oxidation of Sb3+ to Sb5+, while iron oxide behaves as an adsorption site toward both Sb3+ and Sb5+ [12].

Generally, metal oxides are easily recyclable by chemical regeneration – leaching in chemical solvents: acid, organic solvents, or che-lating agents. The main advantages of these adsorbent materials are high pollutant retention ability, exceptional durability, and regeneration capacity.

4.2. Biomass adsorbents

Biomass adsorbents are materials obtained from photosynthetic organisms showing strong capacity and high efficiency in diverse pollutants removal, with minimum residual waste. Adsorbent surface chemistry is the crucial parameter affecting sorption in single and multi-component solutions, where capacity may vary substantially due to the competition between different metal ions. Usage of algae was found to be low-cost and efficient in the sorption process, e.g. *Spirogyra* spp. was detected to efficiently remove Cr^{3+} from water solutions [13]. Recently, the application of a zero-waste system reinforcing the cleaner production concept involved the utilization of various agricultural wastes: orange [14], sugar beet pulp [15], raw corn silk [16], apricot shells [17], etc. for water purification of heavy metal ions. Modified biosorbents exhibit enhanced sorption capacity comparing to the original ones. For example, magnetically modified aloe vera waste biomass showed high sorption capacity even in multi-component solutions [18]. Additionally, biomass feedstock thermochemical decomposition at high temperature in the absence of oxygen leads to the biochar formation – carbonaceous porous material with a surface abundant in nitrogen/oxygen functional groups able to bind various contaminants types. Studies on regeneration and desorption of biosorbents and data on disposal, recycling, and immobilization are limited, reflecting the future research directed towards the improvement of the overall efficiency of this method.

4.3. Nanoadsorbents

Nanomaterials are among the most efficient absorbents for the removal of organic and inorganic pollutants from water due to a broad range of improved physicochemical characteristics: large specific surface area, large number of active sites for interaction, high reactivity, high degree of functionalization, and ease of separation. Carbon-based materials (carbon nanotubes (CNTs), graphite, graphene oxide), metals/metal oxides, polymers, zeolites, and their composites are the most commonly reported nanoadsorbents. CNTs are efficient material for adsorption of diverse pollutants in water, due to high surface area and the versatile possibility of interactions: hydrophobic effect, π–π interactions, hydrogen, and covalent bonding, and electrostatic interactions [19], [20], [21]. Magnetic nanoadsorbents and nanoadsorbents based on polymer fibers and nano-metal/metal oxides are highly efficient for the removal of heavy metal from water [22], [23], [24]. Metal-based nanoadsorbents (iron oxide, titanium dioxide, zinc oxide, and alumina are) show an increase in reaction rate and adsorption capacity with particle size decreases and poses a preferable affinity for heavy metal removal [25], [26]. Additional benefits of magnetic nanoadsorbents (maghemite (γ-Fe_2O_3), hematite (α-Fe_2O_3), and spinel ferrites ($M^{2+}Fe_2O_4$) are that they can easily be separated from reaction media by application of an external magnetic field. Materials, such as nano-Ag, nano-ZnO, nano-TiO_2, CNTs, and polymeric nanoparticles also show good antimicrobial properties and have the potential to replace conventional disinfection methods of polluted water [27], [28]. Although nanomaterials have great potential, they haven't reached large-scale use in wastewater treatment. Currently, the main concern of nanomaterial applications is the toxicity effect, proved for few nanomaterials, meaning that there is a need for additional research with a focus on human health [28].

5. Conclusions and future prospectives

A vast variety of adsorbent types are used for removing pollutants from water, such as oxide-based composites, biomass adsorbents, and nanomaterials, which have proved high potentials in this process. Many of them are able to effectively bind more than one metal simultaneously, adsorb the organic contaminants, or having additional antimicrobic effects. Despite the achieved progress in this field, adsorbents covering versatile pollutants are not synthesized yet. The development of the absorption process is therefore mainly limited to the laboratory stage. Research efforts to improve absorption rates and support scaling to the industrial level should continue, as well as the search for innovative sorbent materials and feasibly sorbent recycling methods.

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