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A Comprehensive Review on Adsorption Techniques for Pharmaceutical Pollutants in Wastewater Treatment

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ABSTRACT

The presence of emergent pollutants in the aquatic environment has raised concerns all over the world because of their adverse effects on the environment and human health. Their elimination becomes a necessity. This article provides a review of the up-to-date research on the treatment of emergent pollutants by adsorption. In this study, we have focused mainly on the elimination of pharmaceutical pollutants from aqueous solutions by deferent adsorbents and comparing their adsorption capacity. Previous studies showed the advantages of using biomaterials and eco-friendly adsorbents to remove these pollutants from wastewater. Most of the adsorbents have shown effective removal of pharmaceutical pollutants. Several parameters influences the adsorption phenomenon such-as pH of the solution, temperature, concentration and nature of pollutant and the dose of the adsorbent.

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Introduction

Lately, novel undesirable components have detected in natural watercourses, directly linked to human and industrial actions. Many of these compounds lack legal regulations but carry the potential for significant harm to aquatic ecosystems when their concentrations become substantial. Traditional wastewater treatment facilities may not consistently succeed in adequately eliminating them, underscoring the necessity for supplementary water treatment methods.

Emerging pollutants are contaminants that have recently identified as a potential threat to the environment and human health, and for which regulatory measures have not yet established. The growing concern over the potential risks of these pollutants has led to increased research efforts to understand better their occce, fate, and effects on the environment and human health. The elimination of the emergent pollutants opens a vast field of scientific research using different techniques such as biological treatment, nanofiltration, Advanced oxidation processes, reverse osmosis, electrocoagulation process, and membrane bioactor, etc. However, adsorption on solid supports remains the most acceptable method in scientific circles because of its simplicity, efficiency, and low cost [1-10].

In the literature, some inexpensive sorbents used to remove emergent pollutants include activated carbon, graphene oxide, biochars, orange residue, chitosan, Also, clays are considered among the best biosorbents for emerging pollutants in aquatic environments [11-17].

In this review, we will study the bioadsorbents as low-cost adsorbents, and their removal performance has been comparing.

Research Significance

The adsorption of pharmaceutical pollutants is becoming an increasing concern due to their impact on the environment and public health. In this context, the search for effective methods to remove these pollutants is crucial. This review focuses on adsorption, a promising process for capturing pharmaceutical pollutants in water. By exploring different adsorbents and evaluating their effectiveness, this study aims to provide practical solutions for eliminating these harmful substances.

Micropollutants in Environment

Micro-pollutants present in the water environment have diverse origins in which domestic wastewater is a principal source of surface water [18].

Heavy Metal

The heavy metal ions, which are inorganic water contaminants, possess highly toxic properties. They are present in aqueous waste streams from various industries, such as metal plating, mining, tanneries, painting, and car radiator manufacturing. They can also originate from agricultural sources where fertilizers and fungicidal sprays are extensively used [19]. The high capacity of these ions to accumulate in living organisms tissues and the human body results in extensive damage to both blood cells and the central nervous system [20].

Organics Molecules

Organics Days

The organic dyes are organic substances that enhance the appearance of marketed products, and they play an important role in synthetic organic compounds. They are widely used in various industries, including printing, food, cosmetics, and clinical applications, as well as for textile dyeing, due to their chemical stability, ease of synthesis, and versatility [21]. Their release into aquatic systems causes environmental damage due to their toxicity. In addition, the elimination of these dyes is of principal scientific interest today.

The Pesticidess

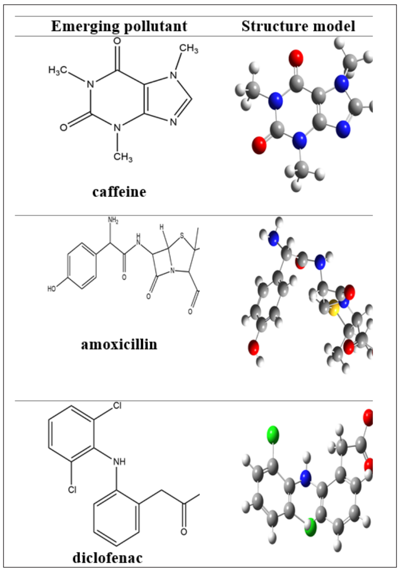
The use of pesticides dates back to the times of Ancient Romans where people used to burn sulfur for killing pests and used salts, ashes, and bitters for controlling weeds. A Roman naturalist urged the use of arsenic as an insecticide [22]. According to ONSSA, there are 1055 commercial specialties of pesticides and 375 active ingredients in Morocco (phytosanitary index 2015). The dispersion of the pesticides in water can generate nuisances as well on the level of their potabilization as of their ecological richness. This diffuse pollution is related to the entrainment of these products by transfer on the surface or in the depth of the waters of irrigation and the rains towards the rivers, the lakes, the water tables, or the seas and the oceans [23]. Among the pesticides, we can distinguish insecticides, herbicides, fungicides.

The Pharmaceuticals Substances

In addition to the principal chemical contaminants in the environmental pollutants, there are the pharmaceuticals substances, which have synthetic substances, which have often been using for medicinal purposes or the depression of modern life. Since then, numerous publications on the subject have shown that most aqueous media contain drug residues [24]. All the different therapeutic classes are found in wastewater, but the quantities are different depending on the consumption, the level of metabolization of the molecule, and the dilution rate in urban sanitation [25]. Conventional wastewater treatment facilities, including activated sludge processes, do not completely remove the pharmaceuticals substances from wastewater: removal rates range from less than 20% to over 80% for some pharmaceuticals substances [26].

The Emerging Pollutants

Emerging pollutants are pollutants of great scientific interest in recent years by researchers, because of their risk on the ecosystem. This type of pollutants includes nanomaterials, nanostructured waste, drugs and their by-products, metabolites of different origins...



Elimination of Emergents Pollutants by Adsorption
Polymeric Adsorbents

Polymeric adsorbents offer significant advantages, such as ease of regeneration, selectivity, and abundance. Several polymeric adsorbents have reported in the literature for the removal of emerging pollutants from aquatic environments, such as chitosan. W.S. Adriano et al prepared chitosan beads for the removal of amoxicillin from aqueous environments. Chitosan showed a high adsorption capacity for amoxicillin, and the adsorption described by the phenomena of internal diffusion and external convection on the chitosan beads. Modeling of the experimental equilibrium data indicates that the isotherm for this system can be considered as Langmuir-type [27]. To improve the capacity of removing emerging pollutants using chitosan, Emanuele et al. prepared composite films by incorporating coffee waste into a chitosan/PVA matrix. Adsorption tests showed an increase in the adsorption capacity of the studied pharmaceutical pollutants for the composite film compared to chitosan. This increase is explained by the increase in active sites on the composite, particularly the functional groups (-OH, -NH, -COOH) of the coffee waste components (cellulose, lignin, hemicellulose, etc.). In another study, Cho et al used the linear free energy relationship (LFER) equation to develop a quantitative structure-adsorption relationship model. They also conducted isotherm experiments to study the affinity between cellulose and several pharmaceutical pollutants. According to this study, they found that cellulose exhibits a high affinity with these pollutants, and that the affinity with cationic pollutants is higher than with neutral and anionic pollutants [28,29].

Activated Carbon

Activated carbons are a porous material with a large specific surface, which makes them a good adsorbent for chemicals, gases, and impurities in water, air, and other liquids. They are obtained from residual biomass such as agri-food waste. shea cakes, coconut shell, date pits [30-32].

Activated carbon has become a commonly employed substance for eliminating micropollutants from aquatic environments. In this context, Flavia et al. tested the elimination of some emerging pollutants (bisphenol A, ethinyltradiol, and amoxicillin) using activated carbon obtained from Macauba biomass. The activated carbon obtained with a specific surface area equal to 907 m2/g showed a high adsorption capacity for the pollutants studied. Based on the study of the pH effect, they concluded that the adsorption mechanism of these pollutants occurs through three mechanisms; (i) π-π dispersion interactions between the aromatic ring of the contaminants and the aromatic structure of the graphene layers, (ii) polar adsorption of the adsorbate by the functional groups of the adsorbent, and (iii) electrostatic interactions between the contaminants and the surface of the activated carbon (Moura 2018). In another study, Karla et al used activated carbon prepared from pineapple leaves for the removal of caffeine from aqueous media. The material showed a specific surface area of 1031 m2/g and a maximum adsorption capacity of approximately 155 mg/g. modelling of the experimental data showed that the adsorption followed the Langmuir isotherm model and pseudo-second-order kinetics. They divided the adsorption mechanism into three regions: the first within the first 2.5 minutes where adsorption occurs through external surface diffusion, the second between 2.5 and 30 minutes where adsorption occurs through intramolecular diffusion, and finally, the third region, which characterized by the appearance of equilibrium after the slowing down of intramolecular diffusion [33]. Finally, it should be noted that the process of regenerating the activated carbon can be expensive and may require specialized technical skills

Bentonite

Bentonite is highly abandoning clay composed mainly of montmorillonite. It has physical and synthetic properties such as small particle size, large surface area, high porosity, and high adsorption capacity, which makes it a good candidate for the micropollutants removal. with a capacity controlled by the nature of the compound and the pore structure, the good adsorption capacity comes from the negative charge, which can be neutralized by the adsorption of positively charged ions [34]. Bentonite has been widely used for the removal of emerging pollutants. Table 1 lists different bentonite-based adsorbents for the removal of pharmaceutical pollutants. Kristia et al studied the elimination of amoxicillin on bentonite and found that the adsorption of amoxicillin is favorable on bentonite with a maximum adsorption capacity at a pH of 2.31. The results of the adsorption tests showed that adsorption strongly influenced by the pH of the solution. At low pH, the functional groups of amoxicillin become protonated, which increases the adsorption capacity. Additionally, modeling of these results shows that adsorption follows the Langmuir model [35]. To study the effect of thermal treatment on adsorption, Oliveira and Al calcined the bentonite at 500°C for 24 hours to increase the material's thermal stability. They then used it as an adsorbent to remove caffeine from aquatic environments. The results showed that thermally modified bentonite can be a good adsorbent for pharmaceutical pollutants, and that caffeine adsorption follows the Langmuir model with a maximum capacity of 0.73 mmol/g at 60°C. Adsorption occurs through a combination of physisorption and ion exchange [36]. In another study, Ghemit et al assumed that the modification of bentonite by active tensions changes the hydrophobic nature of bentonite to hydrophilic, which promotes the adsorption of organic compounds. In their study, they prepared an organobentonite by modifying the bentonite with three different concentrations of cetyltrimethylammonium (0.5; 1; 2 CEC) for the removal of diclofenac and ibuprofen. The experimental results show that the adsorption follows the second pseudo-order kinetic model, and that the Langmuir and Freundlich isotherms describe this adsorption well. Also, the organobentonite with a concentration of 2 CEC is the most effective adsorbent with a maximum capacity of 600 mg/g and 194.9 mg/g for diclofenac and ibuprofen, respectively [37]. Still aiming to improve the adsorption capacity of bentonite, Yi et al synthesized a composite based on bentonite and chitosan for the removal of pharmaceutical pollutants from aquatic environments. Adsorption tests showed that the composite had a much higher adsorption capacity than raw bentonite, which can be explained by the improvement of active sites and the increase in specific surface area of the composite [38-42].

Table 1: Bentonite-Based Adsorbents for the Removal of Pharmaceutical Pollutants

Adsorbent	Pollutant	Capacity of adsorption (mg/g)	Isotherm	Model kinetic	Reference
Bentonite	Amoxicillin	53.9315	Langmuir	pseudo-second order model	[35]
thermally modified bentonite	caffeine	141,75	Freundlich and Dubinin-Radushkevich	---	[39]
Organobentonites	Diclofenac	600,6	Langmuir / freundlich	pseudo-second order model	[37]
	Ibuprofen	194,9			
modified montmorillonite with dodecyl dimethyl benzyl ammonium chloride	Amoxicillin	13.29	freundlich	pseudo-second order model	[40]
	ampicilin	30.86			
L-methionine modified montmorillonite K10	Amoxicillin	647,7	Langmuir	Pseudo-second order model	[41]
Fe2O3-pillared montmorillonite	Diclofenac	103,1	Langmuir	Pseudo-second order model	[42]
bentonite-chitosan composite	Amoxicillin	51.9–86.1	Langmuir	---	[38]
	Ampicillin	66.1–83.3			
	Doripenem	78.4–96.0			

Different Parameters Influencing the Adsorption Capacity

Several parameters influence the adsorption phenomenon such-as:

- The adsorbate concentration: the adsorption capacity increases with the adsorbate concentration increase until the saturation of all the active sites of the adsorbent.
- The granulometry: the smaller the particle size, the larger the specific adsorption surface, and therefore the better adsorption capacity;
- The solution temperature: if the process is endothermic, the adsorption will be favored at high temperature; otherwise will be favored at low temperature;
- The pH of the solution is a crucial parameter to consider when studying adsorption processes, this is because variations in pH can alter the surface charges of adsorbents, and in turn, affect the protonation of functional groups located on the surface of

materials. Therefore, understanding the relationship between adsorbents and adsorbates relies heavily on comprehending the impact of solution pH on adsorption processes.

Isotherm Modelling and Kinetic Studies

Studying the kinetics and adsorption isotherms is a crucial step in understanding the adsorption process. This helps to explain the interaction between the adsorbent and the adsorbate and provides information on the formation of a monolayer or multilayer. In most studies on the removal of emerging pollutants by bioadsorbents, only two-parameter isotherm models were tested. The Langmuir isotherm was found to be the best fit for the experimental adsorption.

Conclusion

The previously mentioned adsorbents seem to possess adequate adsorption properties across a broad range of examined parameters. This review focuses on the removal of emerging pollutants from aquatic environments using various types of adsorbents, such as polymeric adsorbents, activated carbon, and bentonite. The aforementioned adsorbents appear to exhibit satisfactory adsorptive characteristics over the range of parameters studied. Chemical modification has the potential to enhance the adsorption capacity of adsorbents compared to unmodified materials by introducing functional groups and increasing specific surface area. However, further investigation of certain parameters is necessary to gain a better understanding of the adsorption mechanisms of these materials. It is worth noting that in most studies, the Langmuir isotherm model and the pseudo-second-order model were found to best describe.

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