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Review

New approaches on the removal of pharmaceuticals from wastewaters with adsorbent materials

George Z. Kyzas [a,b,*], Jie Fu [c], Nikolaos K. Lazaridis [a], Dimitrios N. Bikiaris [a], Kostas A. Matis [a]

[a] Division of Chemical Technology & Industrial Chemistry, Department of Chemistry, Aristotle University of Thessaloniki, GR-54124 Thessaloniki, Greece
[b] Department of Oenology and Beverage Technology, Technological Educational Institute of Kavala, Kavala GR-65404, Greece
[c] School of Civil and Environmental Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA

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ABSTRACT

This review article summarizes the alternative use of adsorbent materials for treatment of pharmaceutical wastewaters. Pharmaceutical wastewaters are very hazardous and toxic not only for the human but also for environmental life. The existence of various drug pollutants in such effluents surcharges the aqueous media. Therefore, apart from the proposed conventional (until now) methods applied (biodegradation, photocatalysis, ozonation, Fenton process, etc.), the applicability of adsorption as simple and low-cost technique is recently applied. Some of the most important materials discussed in this work are clays, polymers (chitosan), zeolites, various types of (activated) carbons, composite materials (graphene-based), agricultural wastes or soils. The key-factor about the selection of the most suitable adsorbent material has resulted after adsorption experiments varying some major parameters (pH, contact time, initial pharmaceutical compound concentration, ionic strength, etc.). However, the most crucial factor is the adsorption capacity. So, some isotherm models are also commented here (Langmuir, Freundlich, Sips), which predict the maximum theoretical adsorption capacity (Q_m) of each material used.

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Contents

1. Introduction

Pharmaceuticals, newly recognized classes of environmental pollutants, are becoming increasingly problematic contaminants of either surface water or ground water around industrial and residential communities. The presence of pharmaceuticals and personal care products (PPCPs) was first identified in surface and wastewaters in the United States and Europe in 1960s [1]. Concerns about their potential risk were raised in 1999 [2] with the issue attracting considerable interest after the presence of pharmaceuticals in river water was linked to feminization of fish living downstream of wastewater treatment plants (WWTPs) outfalls [3]. Furthermore, a link between a non-steroidal anti-inflammatory drug, diclofenac and the renal failure of vultures contributing to the >95% decline in its population in the Indian subcontinent since the 1990's has been reported [4]. Public awareness was raised after a study showed that organic wastewater contaminants, including PPCPs, were present in 80% of 139 U.S. streams [5]. Although the concentration levels of PPCPs found in the environment are at trace concentrations, their chemical persistence, microbial resistance and synergistic effects are still unknown [6,7], which is a cause for concern. Moreover, low concentrations can elicit adverse effects on aquatic life [8,9].

* Corresponding author at: Department of Oenology and Beverage Technology, Technological Educational Institute of Kavala, Kavala GR-65404, Greece.
E-mail address: georgekyzas@gmail.com (G.Z. Kyzas).

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In general, pharmaceuticals mostly enter water sources through discharge from pharmaceutical industries and from municipal wastewater effluent [10], as well as from hospital effluents. They are classified as recalcitrant bio-accumulative compounds and are thus regarded as hazardous chemicals since they cause contamination of aquatic or terrestrial ecosystems [11]. Unfortunately, many of these pharmaceutical compounds are not completely removed by WWTPs and consequently they have been detected in WWTP effluents, surface waters and, less frequently, in ground and drinking water all over the world [12]. Water containing pharmaceuticals and their transformation products (TPs) need to be treated chemically or physically using an efficient process to protect the environment and the human health against their potential toxicity and other possible detrimental effects.

Several methods have been investigated to remove pharmaceuticals from contaminated water such as biodegradation, photocatalysis, ozonation, and Fenton process [13]. Even though advanced oxidation processes (AOPs) are an efficient way to degrade synthetic contaminants including pharmaceuticals, various intermediates are usually generated during the partial oxidation of complex compounds. Their toxicity can be even higher than that of the parent contaminants. In addition, AOPs are very expensive and operationally complex for the complete degradation of recalcitrant compounds [10].

Physical techniques remain the most appropriate treatment option. Among them, adsorption is the most promising one since it is efficient, simple to design, unaffected by toxicity, and inexpensive [14]. The performance of an adsorption process is affected by an adsorbent's characteristics [15]. Despite the abundance in published works regarding the removal of pollutants with various adsorbents [16–32], there is only few works about the use of adsorption as process for treatment of pharmaceutical compounds.

The aim of this work is to chronically summarize the major works regarding the removal of pharmaceuticals from wastewaters using various adsorbents. Some important parameters are discussed here such as the adsorption capacity of each adsorbent, the optimum contact time between material and drug (kinetic experiments), some thermodynamic criteria about the whole process, potential of reusability, and optimum desorption factors. Additionally, the characterization of the adsorbents reported is commented in order to clearly understand the possible interactions between pharmaceutical compounds and materials.

In adsorption technology, two adsorbent materials cannot be compared (even for the same pollutant) without having the same experimental conditions. Some of the basic parameters which strongly influence the whole procedure are (i) the pH solution, (ii) contact time, (iii) initial pollutant's concentration, (iv) temperature, (v) agitation speed, (vi) volume of adsorbate, (viii) ionic strength of solution, (ix) adsorbent's dosage, etc. It is clear that if any of the aforementioned conditions varies, the experiment will not be the same and consequently none comparison will be correct. Having the above in the mind, the only comparison can be realized for adsorbent/adsorbate systems of the same study. Therefore, it is not correct to say that carbons are better adsorbents than clays or chitosan.

2. Adsorbents for pharmaceutical compounds

2.1. Carbons

Yu et al. studied the removal of some trace pharmaceuticals (PhACs) and endocrine disrupting substances (EDS) during drinking water treatment by adsorption onto activated carbon [33]. The samples of carbon used are two common granular activated carbons (GAC) (coal-based Calgon F400 and coconut-based PICACTIF TE (PICA)) which were evaluated for the removal of ibuprofen, naproxen, carbamazepine, and nonylphenol (NP) in ultrapure water. The initial concentration used for running isotherm experiments was low (10–800 ng/L), because the concentrations of PhACs and EDS are usually lower than 1 μg/L. The equilibrium data were analyzed by both linear and nonlinear regression methods in the forms of Freundlich, Langmuir, and Langmuir–Freundlich (L–F) equations. L–F showed better isotherm data fitting. After experiments, it was found that the adsorption capacity for both carbon samples was much lower for NP than that for naproxen and carbamazepine at low concentrations. Although the PICA showed a somewhat higher capacity than F400 carbon, both would be able to effectively remove the three target compounds at tested concentrations in ultrapure water.

The same research team (Yu et al.) published a similar study [34] using the same carbon samples and drug pollutants (naproxen and carbamazepine) as in the previous study [33]. When determining their isotherms at environmentally relevant concentration levels, it was found that at this low concentration range (10–800 ng/L), removals of the target compounds were contrary to expectations based on their hydrophobicity. Nonylphenol ($\log(K_{ow}) = 5.8$) was most poorly adsorbed, whereas carbamazepine ($\log(K_{ow}) = 2.45$) was most adsorbable. A very interesting approach of this study is the opportunity to compare the adsorbabilities of the target compounds to those of extensively studied micropollutants. This will allow an initial assessment to be made of the appropriateness of inferring the removals of PhACs and EDCs based on the adsorption of other conventional micropollutants. The isotherms of 4 conventional micropollutants – TCE [35], atrazine [36], MIB and geosmin [37] – were generated based on the isotherm data available in the corresponding reference. The three-target compounds exhibited less adsorbability than the other four compounds, especially in the concentration range of 100–1000 ng/L. Atrazine demonstrated a much higher adsorption affinity than all the other compounds. In contrast, the isotherms of the other examined compounds are close but cross each other at an equilibrium liquid phase concentration less than 100 ng/L. As a result, the adsorptions of both MIB and geosmin are expected to be lower than those of naproxen and carbamazepine at liquid phase concentrations of approximately 30–50 ng/L. This point is of practical significance because, like PhACs and EDCs, MIB and geosmin occur in the aquatic environment at the same or even lower concentration ranges. Therefore, it can be preliminarily concluded that the PAC dosage applied for achieving treatment goals of these odorous compounds could provide substantial removals of carbamazepine and naproxen at the same low concentration levels. The reported isotherm concentration range for TCE has usually been much higher than for the other micropollutants examined here. Finally, it seems that none of the selected conventional micropollutants could serve as a reference for the removal of nonylphenol at the low concentrations of interest.

Activated carbons of different sizes were tested as pharmaceutical adsorbents by Ji et al. [38]. Ordered micro- and mesoporous carbons (Micro-C, Meso-C), and nonporous graphite (GR), single-walled carbon nanotube (SWNT), and two commercial microporous activated carbons (AC1, AC2) were tested as adsorbents in three antibiotics (sulfamethoxazole, tetracycline, tylosin). Different adsorption patterns are observed between sulfamethoxazole and the other two antibiotics (tetracycline and tylosin). Adsorption of sulfamethoxazole on the different adsorbents is ordered as follows: AC1, AC2 > Micro-C, Meso-C ≫ SWNT ≫ GR. Alternatively, the adsorption patterns are similar between tetracycline and tylosin, and the adsorption order is shown as Micro-C > Meso-C > SWNT, AC2 ≫ AC1 > GR. The lowest antibiotic adsorption on graphite can be attributed to the smallest adsorbent surface area. However, for other adsorbents the adsorption sequence correlates poorly with the adsorbent surface area. For example, although AC1 has higher BET surface area than SWNT does, adsorption of tetracycline and tylosin is much lower on AC1 than on SWNT. Similar trends are also observed when comparing adsorption of sulfamethoxazole between the two activated carbons and Micro-C. The findings indicate that template-synthesized micro- and mesoporous carbons are promising adsorbents for the removal of antibiotics, particularly, the bulky and flexible-structured compounds, from aqueous solution.

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