INNOVATIVE TECHNOLOGICAL SOLUTIONS FOR REMOVAL OF PHARMACEUTICAL CONTAMINANTS FROM WATER SOURCES

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The waste derived from pharmaceutical products represent a huge worldwide problem. The aim of this paper is to describe, analyze and compare some depollution procedures for such kind of contaminants and to highlight their advantages and disadvantages from various points of view in order to propose concrete cleaning solutions. Classical methods used for contaminant removal from wastewaters in wastewater treatment plants (WTP) and from drinkable water in treatment plants (TP) do not satisfactorily reduce the content of pharmaceutical pollutants (PhP). After an extended analysis of many factors which can be involved in the treatment efficiency, this paper proposes some rehabilitation solutions for existent TP and WTP by adding to the conventional technologies, some operations of advanced treatment. These advanced operations are filtration through semipermeable membranes, i.e., microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), advanced oxidation processes (AOPs), i.e., ozonation, H₂O₂, adsorption on activated carbon (AC). Statistical procedures are applied to compare these removal methods for such type of pollutants and to prove their efficacy. In this context, it is demonstrated that multivariate statistical techniques, combined with water quality indices represent a viable combination to perform accurate monitoring and spatiotemporal analysis of water quality assessment. This work presents concrete solutions for TP rehabilitation in order to comply with regulations in force related to PhP.

Keywords: Pharmaceutical pollutants, Treatment plant, Wastewater treatment plant, Rehabilitation, Semipermeable membranes, Advanced oxidation, Activated carbon.

1 INTRODUCTION

Pharmaceutical pollutants existent in water systems represent a significant problem detected in the last years and they are considered an important class of emerging contaminants. Although the pharmaceutical wastes (due to their enormous amount) are toxic, non-biodegradable and bio-accumulative – properties similar to those of persistent organic pollutants, they are not nominated according to the Stockholm Convention. Pharmaceutical residues were detected in surface and ground waters, wastewaters after processing, and more in drinkable waters as is stipulated by WHO (2012). Unfortunately, traditional WTP are inadequate for the elimination of these contaminants. The negative effect of PhP on human health and on the terrestrial ecosystems is relatively recently established, and detection of these pollutants in aquatic systems implies significant financial efforts and highly qualified personnel.
Lozano et al. (2022), Jiménez-Bambague et al. (2023) and Krishnan et al. (2021) summarize, compare, and discuss appropriate methods to remove pharmaceutical pollutants from wastewaters as electrochemical AOPs, a coupled bio-electrochemical treatment and AOPs, being based on a huge number of studies related to a large pallet of pharmaceutical compounds. Based on the comparative analysis of such studies, we present the disadvantages of classical WTP and TP and propose as a practical alternative their rehabilitation by introducing some innovative technological solutions in order to improve their efficiencies to reduce PhP content from drinkable water.

2 MATERIALS AND METHODS

Systematic analyses on PhP in wastewaters from the city treatment systems are not realized in the literature and only one report on the results of some analyses of natural waters (river flows) appeared in 2013 (Mouele et al. 2021). Data related to PhP in wastewaters from sewage systems come from occasional studies and not from a systematic monitoring. Such data were communicated from different countries and published in an article where the situations related to the presence of pharmaceutical substances in aquatic systems are reviewed (Patel et al. 2019).

2.1 Technologies for Treatment of Wastewaters with Pharmaceutical Contaminants

The efficiency of WT of PhP was calculated with the formula as shown in Eq. (1):

$$\eta = \frac{(c_i - c_e) \cdot 100}{c_i}$$

where \(c_i\) and \(c_e\) represent the pharmaceutical waste concentrations from influent and effluent of WTP.

The current technologies of mechanical-biological WT from existent plants, even those provided with tertiary level, were not particularly devoted to remove pharmaceutical compounds from wastewaters. In the work of Pietrăreanu et al. (2018), the notions “tertiary purification” and “advanced purification” are defined. Tertiary purification includes the processes of denitrification and dephosphorization to assure the conditions indicated by the legislation in force. Advanced WT includes processes such as reverse osmosis (RO), ozonation or other AOPs. Complete design indications for conventional WTP are contained in the publications of Degrémont (2004), and Tchobanoglous et al. (2014). Results of conventional and advanced treatment (WT efficiencies) of the PhP from waste waters related to the elimination (as a whole) of them presented in reports prepared in different countries can be found in WHO (2012).

The decomposition of PhP can be controlled by the design of constructions and installations, by means of the retention time of water in technological objects, seasonal changes, and exploitation conditions. The advanced WT leads to results superior to conventional technologies. The efficiencies in the removal of pharmaceutics can reach 100%. The principal technological operations for advanced WT / treatment are: adsorption on activated carbon (AC), micro-, ultra-, and nanofiltration, RO, and AOPs, i.e., photolysis, ozonation, UV, \(\text{H}_2\text{O}_2\).

2.2 Technologies for Treatment of Waters Devoted to Human Consumption

Concentrations of PhP in drinkable water, data resulted from studies carried out in various countries and presented in technical literature, are much smaller than those determined in natural waters and wastewaters. None of technological operations currently applied in treatment plants (TP), destined for population's water supply, was particularly designed to remove PhP from drinkable water.

Some technological processes / operations currently applied determine the diminution of PhP concentrations in the treated waters, their efficiencies depending on the physical and chemical...
properties of the PhP, as well as of the operating parameters of those installations. The technologies for treatment of surface waters usually contain simple sedimentation of the suspensions (with dimensions greater than 0.2 mm), coagulation of colloidal suspensions, flocculation, sedimentation of flakes, filtration through quartz sand and disinfection. The removal efficiency ($\eta$) represents the percentage of the removed PhP. Two technological schemes for treatment of surface waters and groundwaters are presented in Figs. 1 and 2. Sometimes, these schemes are completed with technological operations like perchlorination or adsorption on AC. Thus, the introduction into the existing treatment technologies of the adsorption on AC can be considered as a rehabilitation measure (by advanced treatment). These operations are filtration through semipermeable membranes (MF, UF, NF, RO), advanced oxidation (ozonation, $\text{H}_2\text{O}_2$), adsorption on AC.

**Fig. 1.** Typical scheme for conventional treatment of surface waters to become drinkable.

**Fig. 2.** Typical scheme for conventional treatment of underground waters to become drinkable.

For an adequate choice of the treatment method, a solution is proposed by using a factorial experiment design, which involves ANOVA multiple factors with or without interaction.

### 3 RESULTS

Some organic compounds, which are soluble in water, with polar molecules (such as sulfamethoxazole, for instance) are not adsorbed on AC, unlike other PhP that can be removed by adsorption. Organic substances, among them the PhP, present even in traces in water, can be effectively removed by AOPs (Huber et al. 2003). MF and UF membranes have no pores of appropriate dimension to retain the molecules of PhP. The high-pressure membranes used in NF and RO give satisfactory results for many PhP (Rosman et al. 2018, Patel et al. 2019). The waters having high concentrations in salts and PhP with small molecular mass may cause big problems for the high-pressure membranes. Artificial infills in soil or riverbeds can be a solution of penetration of feed waters. Artificial infill of waters is based on the phenomenon of self-purification of the soil. This operation is like a slow purification applied in the feed waters treatment. This solution is not appropriate for polychlorinated bisphenol and antiepileptic PhP (Drewes et al. 2003). RO and NF have eliminated more than 85% of NSAIDs from underground waters (Radenović et al. 2008). The adsorption on AC (either dust – DAC or granular – GAC) is frequently applied for removal of organic micropollutants from wastewaters and mainly from drinkable water. Some aspects of the treatment by adsorption for the removal of pharmaceutic contaminants from water will be illustrated below. The efficiencies of the conventional TP in pharmaceutics removal from waters destined for human consumption are given in WHO (2012). Typical technological schemes
for the treatment of waters to become drinkable where some specific operations of advanced treatment are added to conventional operations are presented in Figs. 3 (for surface water) and 4 (for underground waters).

Fig. 3. Typical technological scheme of advanced surface water treatment for drinking water supply.

Fig. 4. Technological scheme of advanced underground waters treatment for drinking water supply with:
- a) very big water hardness;
- b) big water hardness.

The treatment technologies from these two figures are applied considering, besides a big hardness of water, a high content of the organic substances (organic micropollutants, including PhP). In these schemes, the adsorption operation is apparently considered as conventional, but since it is not currently applied in TP, it can be included in the list of technological operations which can be added to satisfy the new quality conditions for drinkable water.

4 DISCUSSIONS

Photocatalysis, although is efficient in the degradation of PhP, is difficult to be applied at large scale since it consumes a lot of energy, involves high operating expenses and many secondary products that limit the application of the operation. The ozonation supposes high energy and operating costs, it is difficult to be applied to big WTP and the secondary products give rise to other difficult problems. Advanced oxidation (H₂O₂, UV, O₃, etc.) although leads to high efficiencies in the removal of pharmaceutics, forms secondary products more toxic than the removed pollutants and also needs a complicated and expensive operation.

Regarding the advanced treatment technologies, the membranes used in RO wear out under the action of oxidant agents and become inactive by biological film coating during operation. Such situations imply that RO cannot be applied at large scale (Homem and Santos 2011). The resulting solution concentrated in salts contains toxic substances, which cause serious problems related to their complete elimination (Homem and Santos 2011). The principal advantages of the inclusion
of the adsorption on GAC in treatment technologies consist in low investment cost, compared to that of filters with membranes, the possibility of removal the organic micropollutants and to reuse the GAC after exhaustion through regeneration (Rivera-Utrilla et al. 2013). Besides AC, other absorbent materials like various polymer resins, biological adsorbents, nanomaterials, and many other solid materials have been tested (Mestre et al. 2007, Tahar et al. 2013, Patel et al. 2019).

Activated carbon materials have been extensively used for the adsorption of PhP from the water (Ahmed et al. 2015, de Andrade et al. 2018). The PhP adsorption on AC depends on their polarity. For instance, carbamazepine is well adsorbed by AC, while sulfamethoxazole does not have a good removal efficacy. Other researched processes such as advanced oxidation, photolysis, ozonation have no big chances to be applied at a large scale in removal of pharmaceutics from water and so we do not present their conclusions in detail. A review of these results is carried out by Patel et al. (2019). The treatment of the drinkable waters by filters with ion exchangers is only used for industrial waters, especially because of secondary effects of application of these processes, problems which imply discharge of wastewater from the regeneration of ion-exchange resins, high costs of investments and exploitation of installations.

4 CONCLUSIONS

This paper is focused on innovative solutions proposed for PhP removal from wastewater and drinkable waters. Usual WTPs are not designed to remove PhP and the conventional plants with primary and secondary levels do not remove, generally, such pharmaceutical micropollutants. TPs which apply disinfection with residual free chlorine can eliminate only around 50% of them.

The advanced treatment techniques (adsorption on AC, MF, UF, and AOPs) can remove efficiently PhP, while NF and RO almost completely. For example, by applying RO, 99% of big PhP molecules are removed. From the technological operations of advanced treatment studied at level of laboratory, pilot, and, in cases of some operations, functional TP, the most attractive are adsorption on GAC, MF, UF, NF and RO. The first technique is considered as being more convenient since the investment costs are lower, smaller operating expenses (power, qualified personnel, reagents), there are no complicated problems to eliminate washing / cleaning of membranes which are sometimes more toxic than the substances dissolved in water and allow the reuse of exhausted absorbent material. TP using membranes are appropriate for small population centers (less than 1000 inhabitants). Taking into account these considerations, this work proposes two models of rehabilitated TP for surface and underground waters, respectively. Design elements and calculation for such a TP will be the aim of another paper. An important decision instrument, which provides a rigorous solution regarding the treatment efficiency is done by ANOVA factorial analysis with or without interaction. Two-factor, three-factor or multiple-factor factorial experiments can realize a more complex analysis of the possibilities to treat several PhP by different methods to choose the most appropriate way for their removal from wastewaters. Rehabilitation of TP and WTP by completion of the existent technologies, as unique measure, does not solve PhP problem, being limited by contaminant removal efficiencies, high costs of investments and exploitation, increased energy consumption. Moreover, TP rehabilitation does not solve completely the problem of diffuse pollutions with pharmaceutics. Increasing production and consumption of medicines multiplies from one year to the next, and thus their increasing impact on the environment and people's health requires intensification / continuation of research on this topic.

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References


