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REMOVAL OF ESTROGENS FROM WASTEWATER BY PHOTOCATALYTIC DEGRADATION

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Introduction

Synthetic estrogens are obtained by chemical synthesis and are widely used for therapeutic or contraceptive purposes. Thus, in addition to the strict use for contraceptive purposes, they are often used to improve menopause symptoms, in the prevention of osteoporosis and hypoestrogenism, in the treatment of metastatic breast cancer, prostate cancer, etc. They are finally eliminated in partially metabolized or non-metabolized form through excretion in urine and feces thus, reaching the municipal wastewater.

Estrogens are also classified as endocrine disruptors, and their presence in natural surface waters causes adverse effects on aquatic organisms. The main route through which estrogens reach natural surface waters is represented by the discharges of insufficiently treated wastewater by conventional techniques. Therefore, the purpose of this work is to make and test a new photocatalytic system for the removal of the estrogenic mixture estradiol valerate/norgestrel from wastewater.

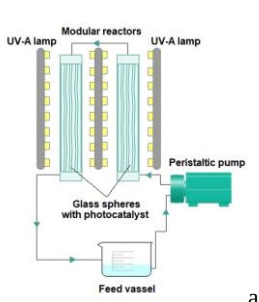
Materials and methods

The photocatalytic system consists of modular reactors (Figure 1a) that use a mixed photocatalyst based on ZnO-TiO_2 deposited on an inert glass support. The photocatalytic modules are operated in the UV-A radiation field, and the aqueous solution with organic substrate (estrogenic mixture estradiol valerate/norgestrel - pharmaceutical formulation) to degrade is continuously recirculated through a feed vessel. The photocatalyst was synthesized by the sol-gel method and deposited on the inert glass support by the hot method, after which it was calcined for two hours at a temperature of 500°C. The degradation of the organic substrate was monitored by taking samples at predetermined times throughout the irradiation period. The concentration of the organic substrate was measured by the chemical oxygen demand (COD) method (closed reflux, colorimetric method).

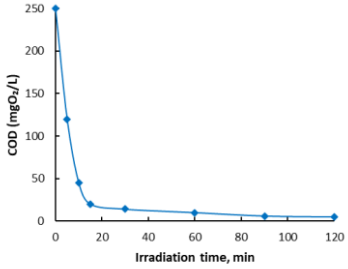
Results and conclusions

The results indicated an efficiency of the photocatalytic degradation more over 98% with only two photocatalytic modules for an irradiation time of two hours and a recirculation flow rate of the working solution of 2 L/h (Figure 1b). It should be noted that the efficiency of the photocatalytic system practically became twice as much after the addition of the second module. This result highlights the fact that the

degradation of the organic substrate depends on the photocatalyst dose inside of the photocatalytic system. Taking into account that the photocatalytic modules are identical both from a constructive and the amount of photocatalyst deposited on the inert glass spheres (arranged in six rows in the modular reactors) point of view, the amount of photocatalyst becomes double when the second modular reactor is added.



a.



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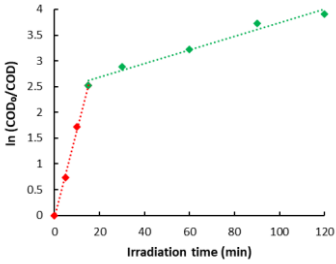

c.

Figure 1. Photocatalytic degradation of the estrogenic mixture estradiol valerate/norgestrel: a. modular photocatalytic system; b. photocatalytic degradation kinetics; c. pseudo-first-order kinetics.

The photocatalytic degradation of the organic substrate follows a pseudo-first-order kinetics in two stages (Figure 1c). The kinetic parameters indicate a rapid degradation of the organic substrate in the first 15 minutes (k_1 = 0.185 min^{-1}), after which the degradation proceeds slowly (k_2 = 0.067 min^{-1}) until almost complete mineralization. This degradation kinetics of the organic substrate highlights the formation of degradation intermediates with high stability to UV-A radiation, but in a reduced proportion because after 15 minutes of irradiation, the effective removal of the organic substrate is 92%.

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