[1,2]Florinela PÎRVU, [1]Cristina Ileana BUTNARIU, [2]Alina Gina CATRINA, [1]Gigel PARASCHIV

PHARMACEUTICAL PRODUCTS REMOVAL FROM WASTEWATER

[1]University POLITEHNICA of Bucharest, ROMANIA
[2]National Research and Development Institute for Industrial Ecology ECOIND, ROMANIA

Abstract: The chemical pollution of water resources with pharmaceuticals is a major challenge facing the humanity in this century. The purpose of this paper was to reviewed methods for removing pharmaceutical products pollutants from wastewater. To assess the efficiency of pharmaceuticals removal from wastewater were presented several methods for removing these residues of drugs. These methods were adsorption on different adsorbent materials, photodegradation and removal during sludge treatment. Among other methods, the adsorption method in the presence of nanoadsorbants is supposed to be one of the best because of its important characteristics. This is due to the remarkable capacity of nanoadsorbants to adsorb a variety of pollutants. Researchers have a special interest in depollution wastewater from the pharmaceutical industry due of their impact on the environment. Water pollution due to drug and pharmaceutical residues is an alarming issue. It is due to the fact that these residues affect human beings and as a result of the degeneration of their biological activities can lead to enzymatic, hormonal and genetic disorders. Pharmaceutical products are widely used in human and veterinary medicine and are present in various samples of water, they can be removed or discharged directly into the domestic wastewater. Moreover, wastewater treatment plants due to insufficient technology to remove these pollutants do not eliminate most pharmaceuticals. Non-eliminated pharmaceutical products get into the groundwater and could be harmful to aquatic organisms even when are present at low concentrations (ng·L-1). Nanomaterials are widely explored as highly efficient adsorbents, photocatalyst and disinfectants for wastewater treatment. Generally, they exhibited various advantages, such as high adsorption capacity, fast kinetics, specific affinity towards targeted pollutants, enhanced photocatalytic response for a broad light spectrum, and strong anti-bacterial activity. The conventional treatment techniques inefficiency for removal pharmaceuticals from wastewater suggests that more attention should be given to for the finding the new treatment processes in order to avoid environmental pollution.
Keywords: pharmaceuticals, pollution, wastewater, nanoadsorbents

INTRODUCTION

Currently literature shows that pharmaceuticals are releasing continuously into the environment in extremely large amounts from various sources such as pharmaceutical industry (waste and wastewater from hospitals), consumption by humans (95% of the dose can be excreted or discharged directly into domestic wastewater), the use of veterinary medicines (Farre M. et. al. 2007, Hong H.N et al. 2007, Imran A. et al, 2016, Renou S. et al, 2008).

Due to the fact that the pharmaceutical products are easily dissolved in aqueous media and do not usually evaporate at normal temperatures or pressures, they can accumulate in the soil and aquatic environments through sewage, treated sludge and irrigation with wastewater not properly treated.

Current research findings clearly demonstrate that current wastewater treatment technologies do not sufficiently remove pharmaceuticals and/or their metabolites and by-products of degradation from wastewater and therefore allow them to enter into surface water, underground water and soil (Kulikowska D. 2008).

Although some pharmaceuticals degrade after consumption or release into the environment, most of them remain unchanged and eventually become persistent in the environment. It is known that most of these chemicals remain bioactive even at extremely low concentrations after excretion from the body or after getting into the landfills and water, have unpredictable biochemical interactions when mixed and may tend to accumulate in the food chain with a negative impact on aquatic organisms and on consumers. As a result, pharmaceuticals, metabolites and their degradation products are of concern for their potential environmental effects (Cilek E.C. et al 2016).

Recent literature indicates that the flow of pharmaceuticals from municipal wastewater treatment plants is an important source of chemical pollution in surface water and seawater (Debska J., et. al. 2004).

Although the reported concentrations of individually reported pharmaceuticals worldwide are low and is not sure that can cause any danger to human health, exposure to a mixture of such compounds can disrupt the human body's balance, increase antibiotic resistance and pose a threat to the health of living organisms.

Some of the potential effects reported on living organisms were: delayed development of fish and frogs, delayed frog metamorphosis, increased feminization of fish populations and a variety of reactions, including modified behavior and reproduction (Shraim A et. al. 2017, Escher B.I., et. al. 2011).

MATERIAL AND METHOD

— Photodegradation

Photocatalysts, particularly those with high stability and activity have been regarded as suitable materials for applications in energy and the treatment of pollutants (Zhang Q. et. al 2018).

Numerous photocatalysts, such as Bi-based photocatalysts, doped TiO_2, Bi_2O_3, Bi_2WO_6, $BiVO_4$ and BiOX have been employed for the photocatalytic degradation of organics in wastewater or the ambient atmosphere (Zhang Q. et. al 2018).

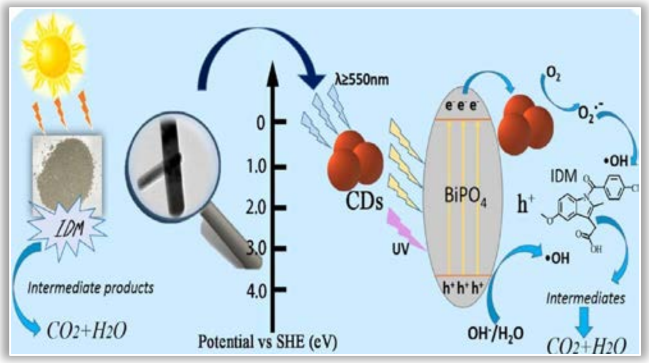

Figure 1- Proposed photocatalytic degradation pathways of indomethacin (IDM) under simulated sunlight irradiation with 3.0 wt% CDBP (novel carbon dots/$BiPO_4$) composites (Zhang Q. et. al, 2018).

Recently, pharmaceutical and personal care products have emerged as pollutants in ambient aquatic environments, which have attracted increasing concern, due to their potentially hazardous effects on ecosystems and humans (Escher B.I., 2011). Because of their stable chemical structures, and thus, they have detected in urban wastewater cycles, and even in drinking water. Some pharmaceuticals have been suspected of directly imparting toxicity to certain aquatic organisms (Rosal R., et. al. 2010)

Several pharmaceutical compounds have been shown to degrade due to the action of sunlight. The most extensively studied of these compounds is the analgesic/anti-inflammatory drug diclofenac, which has been shown to degrade in the aquatic environment due to ultraviolet (UV) light. Other compounds such as the topical antimycotic drugs naftifine, sulbentine, cloxiquin, tolnaftate, and chlorphenesin have also been shown to be light sensitive and an overall elimination rate of 0.03 day^{-1} due to photochemical degradation was observed for triclosan in the epilimnion of Lake Greifensee by Jones et. al. 2005.

Jones et. al. assessed the biodegradability of the clinically important antibiotics cefotiam, ciprofloxacin, meropenem, penicillin G, and sulfamethoxazole using the closed bottle test (CBT). None of the test compounds met the criteria for ready biodegradability. Of all the compounds studied, only penicillin G was found to be biodegradable to some degree, with approximately 27% being removed after 28 days. Even when the test was prolonged to 40 days, the removal rate was only increased to 35% indicating the compound was relatively stable (Jones et. al. 2005).

RESULTS

— Adsorption

In the field of wastewater treatment, nanotechnology exhibited great potential in improving the performance and efficiency of water depollution as well as providing a sustainable approach to secure water supply.

Until now, numerous studies have shown that nanomaterials have vast capability and potential in water, in particular, in the areas of adsorption membrane process 2011), catalytic oxidation (disinfection and sensing (Zhang Y. et. al. 2016).

Adsorbents or membrane based separation process are two most widely used technology for treatment of water and wastewater. Conventional adsorbents often face challenges such as low capacity and selectivity as well as the short adsorption-regeneration cycle, which significantly reduced the cost effectiveness of the adsorbants. Nanomaterial based adsorbants, i.e., nanosized metal or metal oxides, carbon nanotubes (CNTs), graphene and nanocomposites, often feature large specific area, high reactivity, fast kinetics and specific affinity to various pollutants. Their adsorptive performance towards certain pollutants is sometimes several magnitude higher than conventional adsorbents. Besides adsorption, membrane separation is also a key module in the treatment stage, enabling water reclamation from unconventional water sources such as municipal wastewater (Zhang Y. et. al. 2016). Nanocatalysts of high surface-to-volume ratio showed significantly enhanced catalysis performance over their bulk counterparts.

Additionally, the band gap and crystalline structure of the nanosized semiconductors exhibited size-dependent behavior. Their electron hole redox potential and photo-generated charge distribution varied with varying sizes (Zhang Y. et. al. 2016),

Separating and recovering nanomaterials from water after reaction has long been a technical bottleneck to overcome. Magnetic nanosized iron oxide adsorbants offered a viable and convenient solution by utilizing an external magnetic field (Hua et al., 2012). Another important magnetic adsorbent is nanosized magnetite considering its low cost, simple manipulation and environment-friendly properties.

Nanosized manganese oxides (NMnOs) exhibited superior adsorptive performance towards certain pollutants than other metal oxides because of its polymorphic structures and higher specific area (Tesh et al., 2014).

— Removal during sludge treatment

Many pharmaceuticals are not thermally stable and so might be expected to break down during processes such as composting due to heat (as well as chemical and biodegradation). Guerin investigated soil composting as an alternative to incineration for the treatment of a silty clay soil that had become polluted with residues of Probenecid (an antigout drug) and Methaqualone (a barbiturate substitute no longer available due to harmful side effects). In pilot scale trials, Probenecid was reduced from 5100 mg kg^{-1} to <10 mg kg^{-1} within 20 weeks during mesophilic treatments. The study also confirmed that thermophilic composting was effective under field conditions (Guerin, T.F, 2001).

CONCLUSIONS

The results sustain further research on this subject of interest by investigating different types of pharmaceutical products with some removal techniques.

Pharmaceuticals are used in large amounts in human medicine and reach the aquatic environment mainly through sewage treatment systems, where their concentrations can reach micrograms per liter levels. Some predictions can be made based on their physical and chemical properties, but their fate and behavior are not clear. There is little experimental evidence showing levels of pharmaceutical compounds in sewage effluent or sludge and even less showing they should be of concern. However, their biological activity alone may support ecotoxicity assessments of chemicals with high production volumes, especially in view of the increasing importance of freshwater resources and use of drug compounds.

Nanomaterials are widely explored as highly efficient adsorbents, photocatalyst and disinfectants for water treatment. Generally, they exhibited various merits, such as high capacity, fast kinetics, specific affinity towards targeted pollutants, enhanced photocatalytic response for a broad light spectrum, and strong anti-bacterial activity. They are arguably the most promising candidate for the development of next generation wastewater treatment technology.

In this paper we presented three removal techniques for pharmaceutical products from wastewater. The most promising technique is the adsorption of pharmaceutical products onto nano adsorbants.

Despite the increasing research activities in this field, there is still a considerable need for future work and further investigation in order to assess the significance of pharmaceutical products in terms of their persistence and potential.

Note:

This paper is based on the paper presented at ISB-INMA TEH' 2018 International Symposium (Agricultural and Mechanical Engineering), organized by Politehnica University of Bucharest – Faculty of Biotechnical Systems Engineering (ISB), National Institute of Research-Development for Machines and Installations Designed to Agriculture and Food Industry (INMA) Bucharest, The European Society of Agricultural Engineers (EurAgEng), Society of Agricultural Mechanical Engineers from Romania (SIMAR), National Research & Development Institute For Food Bioresources (IBA), University of Agronomic Sciences and Veterinary Medicine Of Bucharest (UASVMB), Research-Development Institute for Plant Protection (ICDPP), Hydraulics and Pneumatics Research Institute (INOE 2000 IHP), National Institute for Research and Development in Environmental Protection (INCDPM), in Bucharest, ROMANIA, between 01–03 November, 2018.

References

[1] Farre M., Petrovic M., Barcelo D., Recently developed GC/MS and LC/MS methods for determining NSAIDs in water samples, Anal Bioanal Chem. 2007, 387, pp. 1203–1214;

[2] Hong H.N, Kim H.N, Park K.S, Lee S.K, Gu M.B., Analysis of the effects diclofenac has on Japanese medaka (Oryzias latipes) using real-time PCR., Chemosphere 2007, 67, pp 2115–2121;

[3] Imran A., Zeid A.O., Abdulrahman, Synthesis of composite iron nano adsorbent and removal of ibuprofen drug residue from water, Journal of Molecular Liquids, 2016, 219, pp. 858–864;

[4] Renou S., Givaudan J. G., Poulain S., Dirassouyan F. and Moulin P., Landfill leachate treatment: review and opportunity, Journal of hazardous materials, 2008, 150(3), pp. 468-493;

[5] Kulikowska D.and Klimiuk E., The effect of landfill age on municipal leachate composition, Bioresource Technology, 2008, 99 (13), pp. 5981-5985;

[6] Cilek E.C. and Karaca, S. Effect of nanoparticles on froth stability and bubble size distribution in flotation, International Journal of Mineral Processing, 2015, 138, pp. 6 - 14;

[7] Imran A., Aboul-Enein H.Y., Kümmerer K., Analyses of drugs and pharmaceuticals in the environment, in: B. Xing, N. Senesi, P.M. Huang, Biophysico-Chemical Processes of Anthropogenic Organic Compounds in Environmental Systems, 2011, IUPAC Sponsored Book SeriesWiley, USA 2011, pp. 439–462;

[8] Debska J., Kot-Wasik A., Namiesnik J., Fate and analysis of pharmaceutical residues in the aquatic environment, Crit. Rev.Anal. Chem. 2004, 34 (1) pp. 51–67;

[9] Shraim A., Diab A., Alsuhaimi A., Niazy E., Metwally M., Amad M., Sioud S., Dawoud A., Analysis of some pharmaceuticals in municipal wastewater of Almadinah Almunawarah, Arabian Journal of Chemistry 10, 2017, pp. S719–S729;

[10] Escher B.I., Baumgartner R., Koller M., Treyer K., Lienert J., McArdell C.S., Environmental toxicology and risk assessment of pharmaceuticals from hospital wastewater, Water Res. 2011, 45(1), pp 75–92;

[11] Rosal R., Rodrguez A., Perdign-Meln, J.A., Petre, A., Garca´ a-Calvo,E., Gmez, M.J., Aguera, A.;

[12] Fernandez-Alba, A.R., Occurrence of emerging pollutants in urban wastewater and their removal through biological treatment followed by ozonation, Water Res. 44 (2), 2010, pp. 578–588;

[13] Zhang Q., Chen P., Zhuo M., Wang F., Su Y., Chen T., Yao K., Cai Z., Lv W., Liu G., Degradation of indometacin by simulated sunlight activated CDs-loaded $BiPO_4$ photocatalyst: Roles of oxidative species, Applied Catalysis B: Environmental, 2018, 221, pp. 129-139;

[14] Jones O. A. H., Voulvoulis N. and Lester J. N., Human Pharmaceuticals in WastewaterTreatment Processes, Critical Reviews in Environmental Science and Technology, 2005, 35:401– 427;

[15] Zhang Y., Wu B., Xu H., Liu H., Wang M, He Y, Pan B., Nanomaterials- enabled water and wastewater treatment, NanoImpact 3-4, 2016, pp. 22-39;

[16] Guerin, T.F. Co-composting of pharmaceutical wastes in soil, Lett. Appl. Microbiol. 33, 256–263, 2001;

[17] Hua, M., Zhang, S., Pan, B., Zhang, W., Lv, L., Zhang, Q., Heavy metal removal from water/ wastewater by nanosized metal oxides: a review. J. Hazard. Mater. 2012. 211-212, 317–331;

[18] Tesh, S.J., Scott, T.B., Nano-composites for water remediation: areview. Adv. Mater. 2014, 26 (35), 6056–6068.

ISSN: 2067-3809