

A Review of Treatment and Sampling Analysis Methods for Pharmaceuticals and Personal Care Products

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Abstract

This article reviews the commonly used methods of removing, sampling and analyzing pharmaceuticals and personal care products (PPCPs), and looks forward to the future research and development of pharmaceuticals and personal care products (PPCPs). A large amount of data shows that PPCPs, as a class of emerging pollutants, will cause serious harm to the ecological environment and human health. Although there are not many reports on the detection and treatment of PPCPs in surface water, drinking water and sewage, due to the greater potential harm of PPCPs, sufficient attention should be paid to the research and treatment of PPCPs. This article describes PPCPs in detail.

Keywords

Pharmaceuticals; Personal Care Products; Processing Methods; Sampling and Analysis.

1. Introduction

Pharmaceuticals and personal care products (PPCPS) are a class of "new" chemical substances that have received widespread attention from the scientific community and the public since 2000. This concept was first proposed in 1999 by Daughton. It includes human and veterinary medicines (prescription and over-the-counter drugs and biological agents), diagnostics, health products, musk, cosmetics, sunscreens, disinfectants, and Various ingredients (such as excipients, preservatives, etc.) added during the production of PPCPs. PPCPs can cause serious harm to the environment and organisms. CD Daughton's research found that PPCPs can enter the aquatic environment through a variety of ways and cause pollution to the aquatic environment. This pollution will slowly accumulate until it causes irreversible changes. G Zhu's research shows that pentachlorophenol presents a high risk in certain effects, such as triclocarban which presents a high risk to the cell growth, death and reproduction of aquatic organisms. Triclocarban, diclofenac, ibuprofen and triclosan have adverse effects on the aquatic organisms in the Pearl River. The pollution of PPCPs is widespread worldwide, and there are reports related to the pollution of PPCPs in various countries. SA Aaberg collected river sediment samples from two urban streams to investigate its toxicity to benthic organisms. The results show that the concentration of pentachlorophenol is in the range of 50-200 ng/g, and the comprehensive contribution rate to the total toxicity of sediment is as high as 8.2%. NA Miasoedova et al. measured the content of pentachlorophenol in the southern part of Lake Michigan and found that it is ubiquitous and persistent in Lake Michigan. JW Kim used liquid chromatograph and tandem mass spectrometer to detect 13 kinds of PPCPs at 5 sampling points along the Wanjing River. The data shows that the highest concentration of PPCPs downstream of the wastewater treatment plant means that the wastewater treatment plant's removal efficiency for PPCPs is insufficient.

The core technology of urban sewage treatment plants is biological treatment technology, which mainly uses microbial metabolism to consume organic pollutants in wastewater. However, traditional biological treatment technology can only remove easily biodegradable

organic pollutants, and most PPCPs tend to have biological toxicity or bioinhibition, complex molecular structure, unique biochemical properties (insoluble and low adsorption performance). At present, the treatment methods for this type of refractory sewage are mainly physical and chemical treatment methods. Commonly used physical and chemical methods are: coagulation sedimentation, adsorption method, advanced oxidation technology, membrane filtration and so on.

Because this article reviews several commonly used methods of degradation and sampling and analysis of PPCPs, it provides a reference for china to carry out relevant research and establish the ecological risk assessment of drug pollution in the water environment.

2. Treatment methods of PPCPs

Because PPCPs have specific biological activities, certain bioaccumulation and genetic effects, they will have a profound and irreversible impact on the water environment. At present, the traditional domestic water treatment process has a poor removal effect on PPCPs, and the research on its degradation started late, with fewer methods, mainly adsorption, ultraviolet photolysis, biological ponds and other methods, but these methods have complex operations, Disadvantages such as high energy consumption, high cost and low mineralization efficiency. Therefore, the research and development of simple, cost-effective, efficient and stable PPCPs removal technology is an important frontier topic in the field of water treatment at home and abroad. The following focuses on the application of several commonly used physical, chemical and biological methods in the treatment of wastewater containing PPCPs.

2.1. Physical treatment

Physical methods to remove PPCPs in water and wastewater mainly include adsorption and membrane separation methods.

Huang et al. used cotton as a biological template to prepare biomorphic nano-hydroxyapatite (HAP) by co-precipitation, and used it to adsorb and remove oxygen fluoride in representative drugs and personal care products (PPCPs) Floxacin (OFL) and Triclosan (TCS). The surface area and porosity, crystal phase, functional group, morphology and microstructure of the synthesized HAP were characterized by Brunauer-Emmett-Teller isotherm, X-ray powder diffraction, Fourier transform infrared spectroscopy, scanning electron microscope and transmission electron microscope. In batch experiments, the effects of initial pH, ionic strength, initial concentration, contact time and temperature on the removal of PPCPs were studied. The adsorption rate of OFL and TCS is very fast, almost completed within 50 minutes. Kinetic studies have shown that the adsorption processes of OFL and TCS follow pseudo-first-order and pseudo-second-order models, respectively. Compared with other adsorbents, bio-form HAP has the advantages of environmental friendliness and large adsorption capacity, showing its application potential in the removal of PPCPs.

Li Jian et al. used bismuth oxyhalide (BiOX , $X=\text{Cl}, \text{Br}, \text{I}$) as adsorbents or photocatalysts to study the effectiveness of BiOX adsorption/photocatalytic removal of typical PPCPs in water. Experiments show that the combination of $\text{BiOBr} + \text{PMS}$ has the best effect on the removal and degradation of CBZ, which can completely remove CBZ at a concentration of $5\mu\text{M}$ within 5 minutes. It is also found that the combined process of $\text{BiOCl} + \text{PMS} + \text{UV}$ treats the TOC of a variety of difficult-to-degrade PPCPs, and the removal rate exceeds 90%.

Membrane separation is a water treatment method that uses porous or non-porous membranes to trap pollutants in water to achieve a purification effect. The influencing factors of membrane separation and removal of PPCPs mainly include the characteristics of membrane materials, operating conditions, and the properties of PPCPs. Yoon et al. studied the effect of UF and NF on the removal of PPCPs, and found that the removal rate of NF on PPCPs was 44% to 93%, and the removal rate of UF was about 40%.

2.2. Chemical treatment

Chemical methods can destroy the molecular structure of organic pollutants and improve their biodegradability, which has attracted widespread attention in the removal of toxic organic pollutants.

DD Borikar's research shows that traditional treatment methods have a limited removal rate of selected PPCPs and EDCs (as a group) (average 30%). On the contrary, ozone/H₂O₂ plus conventional treatment is the most effective process to remove selected PPCP and EDCs (about 97% on average), followed by ozone and conventional treatment, which are also very effective, but the removal rate is slightly lower (average 95%). In general, regardless of the raw water quality, ozone/H₂O₂ or ozone plus conventional treatment are very effective. However, the effect of conventional treatment plus UV/H₂O₂ AOP differs depending on the raw water quality, resulting in lower raw water quality that contains higher organic matter, bicarbonate, carbonate, and particulate matter. The efficiency of the lower raw water quality is reduced. The average removal rate of PPCPs and EDCs by conventional UV/H₂O₂ treatment is about 86%. The experiment of ozone or ozone/H₂O₂ plus SSF also has a relatively high removal rate of the target pollutants. On average, the combined process has a removal rate of about 95-100% for PPCPs and EDCs. In contrast, the removal rate of PPCPs and EDCs by independent ozone or ozone/H₂O₂ is about 77%.

Deng Jianping's research and experiment results show that the combined process of BiOCl + PMS + UV can increase the mineralization degree of CBZ to about 90% within 120 min under the luminous flux of 550 μ W/cm², which greatly improves the mineralization rate. Using EPR to detect the experimental mechanism, it was found that hydroxyl radicals·OH, etc. played a major role in it, and LC-MS was used to detect the reaction intermediate products of CBZ during the reaction, and on this basis, the CBZ mineralization degradation pathway was speculated. In addition, the method was applied to the degradation studies of a variety of common PPCPs in single and mixed solutions, and it was found that the combined process of BiOCl + PMS + UV has a TOC removal rate of more than 90% for a variety of difficult-to-degrade PPCPs, so it is beneficial. The promotion of this method in practical application.

Yang Mengli studied the removal of typical PPCPs through the joint action of natural manganese ore and microorganisms. Manganese minerals are abundant in nature and widely distributed. Manganese minerals generally have a layered or pore structure, with the characteristics of low charge zero point and large surface charge, so they have good adsorption and catalytic performance. At the same time, because of the high valence of manganese in many manganese oxides in nature, they also have good oxidation properties. Therefore, manganese minerals have great potential and research prospects in removing PPCPs. At the same time, studies have shown that dissimilated metal-reducing bacteria have the ability to use organic matter as electron donors and metal oxides as electron acceptors to reduce metal substances and degrade organic matter. This is important for the degradation and ecological restoration of PPCPs pollution in the water environment. significance.

2.3. Biological treatment method

Biological treatment methods include aerobic treatment, anaerobic treatment and facultative treatment. It is the main process of wastewater treatment and plays an important role in water pollution control.

Activated sludge method is a typical aerobic biological treatment method, mainly under the conditions of artificial oxygenation, the sewage and various microbial flora are cultivated to form activated sludge, and the biological aggregation, adsorption and oxidation of the sludge are used. The process of degradation of organic pollutants in water. The traditional activated sludge method is affected by temperature and the types of PPCPs in the process of processing PPCPs.

Biological treatment technology is the most commonly used sewage treatment technology in china, and it is the main method for sewage treatment plants to degrade PPCPs. The anaerobic-anoxic-aerobic treatment combined membrane bioreactor (A2O-MBR) was used to treat domestic sewage. It was found that the removal efficiency of PPCPs reached 86.85% after the A2O-MBR process. Wang Zhuo's research on Shenzhen sewage treatment plant proved that the commonly used reclaimed water treatment process in Shenzhen, namely fiber filtration/chlorine disinfection process, can remove most PPCPs less than 10%. The overall removal rate of chlortetracycline by the traditional biopharmaceutical wastewater treatment process is about 92%, while the combined process of membrane bioreactor (MBR) and ozone/ceramic membrane formation has a removal rate of 99% for chlortetracycline. For municipal sewage, the membrane bioreactor (MBR) has a significantly higher removal effect on most PPCPs in the sewage than the traditional sewage treatment process.

3. PPCPs sampling and analysis methods

3.1. Sampling method recommendations

Ye Pengxian enriched PPCPs from the collected water samples by means of solid-phase extraction, and concentrated by nitrogen blowing to obtain the enriched methanol-aqueous solution. After measuring the data, the data of each sampling point was obtained. After integrated analysis, the concentration of PPCPs was obtained with the concentration of the Xinxing River Basin. The law of change.

Wang Wei learned from the design of the existing polar organic matter passive sampler (POCIS) in foreign countries, researched and established passive sampling in-situ enrichment equipment suitable for the monitoring of PPCPs in groundwater in china, and carried out in-situ correction experiments to determine the active and passive sampling of groundwater 12 To analyze the feasibility of passive sampling applied to the monitoring of PPCPs in groundwater.

Huang Sicong established a deep eutectic solvent-high performance liquid chromatography method for the extraction and determination of three kinds of PPCPs in environmental water samples. By optimizing the pretreatment conditions, the three PPCPs (chloramphenicol, chlorphenesin and naproxen) were extracted with choline chloride-ethylene glycol deep eutectic solvent for 5 minutes under ultrasonic power of 120 W. , Centrifugation at 9000 r/min for 10 min to enrich and extract.

Huang Ke established Dispersive Solid Phase Extraction-Ultra Performance Liquid Chromatography Tandem Mass Spectrometry (dSPE-UPLC-MS/MS) for the determination of sulfamethoxazole (SMZ), trimethoprim (TMP) and tylosin in aquatic products (TYL) and Triclocarban (TCC) and other two types of 4 kinds of PPCPs residue determination methods.

3.2. Analysis method recommendations

Based on solid phase extraction (SPE) and liquid-mass spectrometry (HPLC-MS/MS), Zhang Lian established a method for the simultaneous detection of 19 levels of PPCPs in drinking water, which affects the efficiency of pretreatment and the accuracy of liquid quality detection. The various factors and conditions of the degree have been optimized. The minimum detection limit range of the optimized determination method is 0.06~16ng/L, and the recovery rate of standard addition is 37.69%~118.83%. The time-varying law of PPCPs pollution in the water supply pipe network was studied. A total of 13 PPCPs pollutants were detected during the monitoring period, and their concentration range was ND~17.65ng/L.

Lin Lifeng used an ultra-high performance liquid chromatograph and a triple quadrupole mass spectrometer to establish a liquid chromatography-mass spectrometry detection method for 79 kinds of PPCPs in 6 categories. This method has been applied to the quantitative analysis of

PPCPs in environmental samples, and the detection limit and stability meet the needs of actual sample analysis.

Lu Yan used solid-phase extraction technology to pre-treat the samples, instead of traditional liquid-liquid extraction, and established optimized GC-MS analysis conditions for synthetic musk compounds. This method has short detection time, low impurity interference, high analytical sensitivity, and is suitable for simultaneous analysis of polycyclic musks, nitromusks, and per-deuterated compounds.

Gao Jie introduced the isotope internal standard and further developed a more accurate and stable method for the precise determination of PPCPs. Based on the international mainstream solid phase extraction liquid chromatography tandem mass spectrometry analysis method, through the system optimization of the water bottle material, solid phase extraction column, liquid chromatography mass spectrometry parameters, etc., the 38 kinds of PPCPs that are common in my china's water bodies have been established. (Including 16 kinds of human and 22 kinds of veterinary PPCPs) analysis methods. The domestic solid-phase extraction column Cleanert PEP-2 was used in the screening to replace the imported Oasis HLB column, which greatly reduced the analysis cost. The method was applied to actual water samples such as drinking water, river water, and sewage to investigate its applicability. The results showed that the relative standard deviation of the parallel experiment was less than 30%, and there was no background higher than the quantitative limit of the method in the blank experiment, indicating that the established The analysis method can be well applied to the monitoring of various types of water bodies.

4. Conclusions and prospects

A large amount of data shows that PPCPs, as a class of emerging pollutants, will cause serious harm to the ecological environment and human health. Although there are not many reports on the detection and treatment of PPCPs in surface waters, drinking water and sewage, due to the greater potential harm of PPCPs, the research and treatment of PPCPs should be paid enough attention, and many work needs to be further carried out.

- (1) The migration and transformation law of PPCPs pollutants in the environment and their hazards;
- (2) In-depth research is needed on the operating conditions and influencing factors of various treatment methods;
- (3) The effects of various treatment methods on PPCPs pollutants The removal mechanism is not very clear at present and needs further discussion and research.

Although the various methods of processing PPCPs in china at this stage have certain effects, they also have some limitations. The physical method is simple and easy to implement, but it only transfers the pollutants from the liquid phase to the solid phase to achieve the enrichment of the pollutants, and does not completely eliminate the pollution of PPCPs; the chemical method has become a research hotspot in the field of water pollution control, with pollutants It has the advantages of high removal efficiency, rapid reaction and thorough degradation of pollutants, but the operating cost is relatively high and the operation is more complicated. Biological treatment is the most common method used to degrade organic pollutants, but the removal rate of difficult-to-degrade toxic organic pollutants is not high. During the degradation process, some intermediate products are more toxic than the parent body, which poses a serious impact on the safety of china's water environment. serious threat. Therefore, it is particularly important to find an efficient, green and economical degradation technology.

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