



Emerging Pollutants: Protecting Water Quality for the Health of People and the Environment

Emerging Pollutants – Pitfalls in their Removal – A Case Study

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Overview on Emerging Pollutants

- ❑ The US EPA (United States - Environmental Protection Agency) defines emerging pollutants as new chemicals without regulatory status and which impact on environment and human health are poorly understood.
- ❑ Emerging pollutants are chemical substances that have recently been identified as potentially harmful to human health and the environment. These pollutants may be found in a variety of sources, including industrial and agricultural runoff, waste products, and consumer products.
- ❑ Are not strictly regulated but have the potential to cause harmful effects to human health or the environment
- ❑ Pharmaceuticals and personal care products (PPCPs) are widely used all over the world with enormous diversity.

Overview on Emerging Pollutants

- More than 3000 pharmaceutical products are used in medicines such as anesthetics, antibiotics, contraceptives, lipid regulators, calmatives, and impotence drugs
- Some PPCPs are endocrine disrupting compounds (EDCs)
- Per- and polyfluoroalkyl substances (PFAS)
- Veterinary pharmaceuticals
- Micro-nanoplastic
- Pesticides and herbicides



Origins and Fate of PPCPs in the Environment

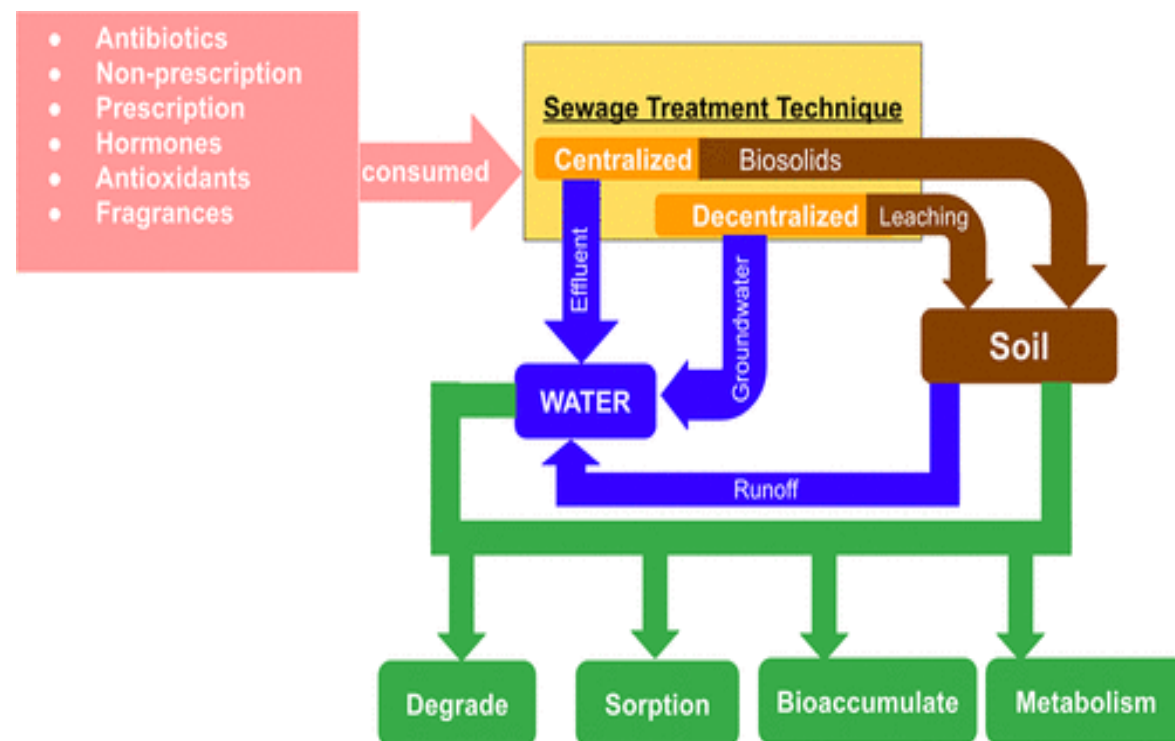
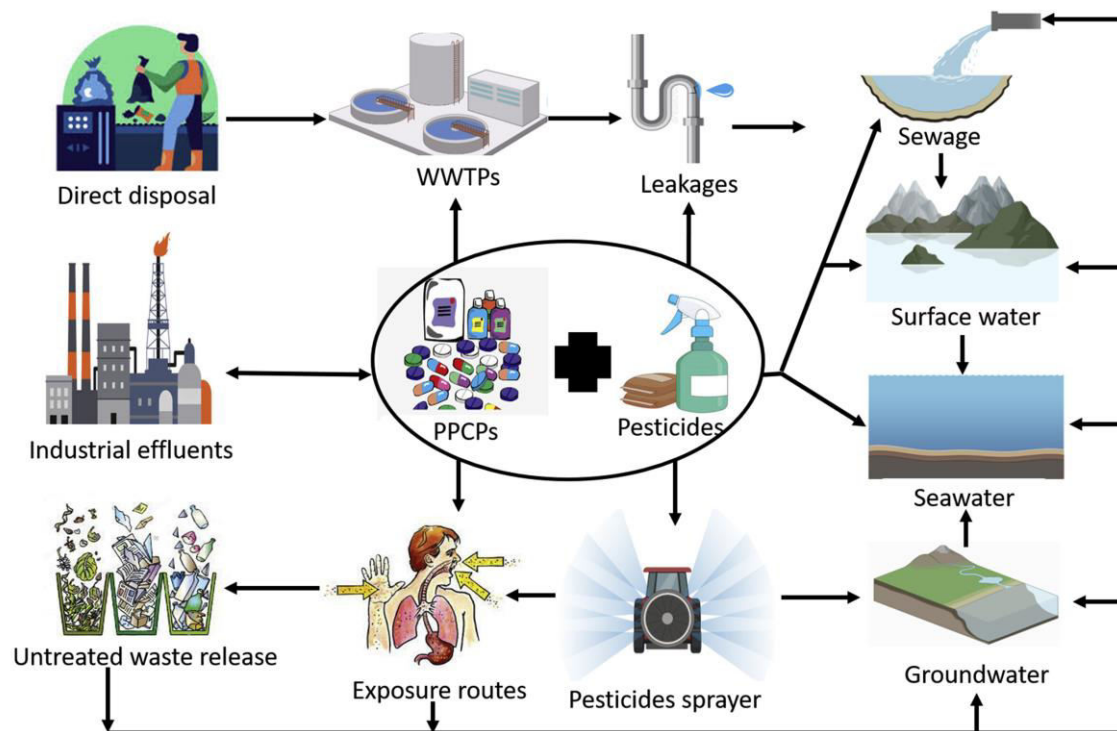
- ❑ Pharmaceutical (medicines) : These substances are taken by humans during their medical treatment and the excess are discharged into wastewater and aquatic environment either from human bodies after metabolism or by direct disposal in toilets.

- ❑ Personal care products are regularly discharged into wastewaters and the aquatic environment during showering and bathing.

- ❑ Other common routes:
 - Emerging pollutants can enter water systems through inappropriate disposal, landfill leaching, agricultural runoff, drain water, livestock and veterinary wastes.

 - PPCPs and EDCs production industries, domestic and industrial wastewater effluents, hospital waste and wastewaters.

Origins and Fate of PPCPs in the Environment



<https://doi.org/10.1016/j.heliyon.2022.e09143>

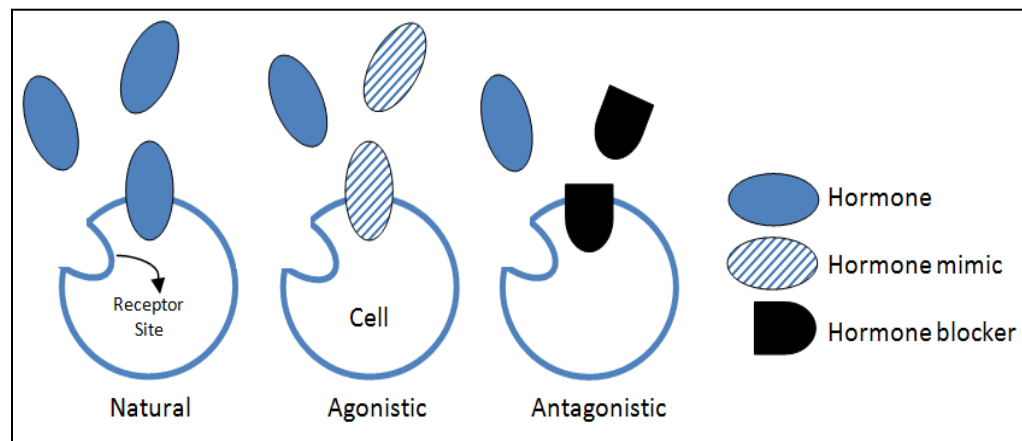
<https://doi.org/10.1021/acs.est.9b02966>

Adverse effects of emerging pollutants

- Emerging pollutants can accumulate in aquatic creatures' bodies which enter the food chain and are then consumed by humans and can adversely affect the environmental species even at concentrations of ng/L and $\mu\text{g/L}$.
- Some personal care products are endocrine disrupting compounds. EDCs are also extensively found in pesticides, steroids, metals, and perchlorate.
- EDCs are chemicals which can alter the hormonal systems of organisms and their disruption endpoints are classified to be estrogenic, androgenic, or thyroidal.
- EDCs may reduce fertility, cause feminization and anomalies in the reproductive organs, as well as changes in the sexual behavior of some aquatic creatures such as fish, algae, frogs, etc.

Adverse effects of emerging pollutants

- ❑ For example, metformin which is consumed regularly by diabetes patients is one of the most found pharmaceuticals in treated wastewater effluents.
- ❑ Although it is non-hormonal pharmaceutical, it shows similar effects on fish to estrogens from birth control medications and acts as an endocrine disrupting compound.



Agonistic and antagonistic responses of EDCs in a cell

<https://doi.org/10.2166/wh.2009.021>

EDCs can cause agonistic effects where they act as hormone mimic compounds by binding to the hormone receptor sites in a targeted cell and thus activating a response.

They can alternatively cause antagonistic effects which can act as hormone blockers and avoid any response by blocking the receptor sites from the natural hormone's interactions

Adverse effects of emerging pollutants

Toxicity effects (Health):

- Neurotoxicity (harm to the nervous system)
- Genotoxicity (harm to DNA)
- Carcinogenicity (ability to cause cancer).

Environmental impacts:

- Negative impacts on the environment
- Contaminating water and soil, harming wildlife,
- and reducing biodiversity

Antibiotic Resistance

- A serious public health problem, as it can make it more difficult to treat infections and can lead to the spread of antibiotic-resistant bacteria.

Categories	Sources	Human health Impact	Environmental Impact
Polycyclic aromatic hydrocarbons (PAHs)	Found in asphalt used in road construction, medicines, dyes, plastics, and pesticides. They can also be found in substances such as crude oil, coal, coal tar pitch, creosote, and roofing tar.	<ul style="list-style-type: none"> • Carcinogenic and potential neurotoxin. 	<ul style="list-style-type: none"> • Have moderate to high acute toxicity to aquatic life and birds. • In high concentrations in soil, can have adverse effects on terrestrial invertebrates including on reproduction, development, and immunity, and may cause tumours.
Pesticides	Agricultural run-off and urban green spaces and parks (include herbicides and insecticides).	<ul style="list-style-type: none"> • Short-term impacts such as headaches and nausea. • Chronic impacts such as cancer, reproductive harm, and endocrine disruption. 	<ul style="list-style-type: none"> • Can contaminate soil, water, turf, and other vegetation. • Can cause mortality in insects and weeds. • Toxic to other organisms including birds, fish, beneficial insects, and non-target plants.
Environmental oestrogens	Synthetic chemicals found in food, animals and plant products and some household items.	<ul style="list-style-type: none"> • Have been linked to breast cancer in women and prostate cancer in men. • Oestrogen has a wide range of effects on the body and brain, including on emotional processing via neuropsychological factors. 	<ul style="list-style-type: none"> • Impact fish physiology and can affect reproductive development in both domestic and wild animals. • Can mitigate the effects of other environmental stresses on the plant.
Phthalates	Industrial chemicals used to soften PVC plastic and as solvents in cosmetics and other consumer products.	<ul style="list-style-type: none"> • Damage to the liver, kidneys, and lungs. • Damage the reproductive system, and can cause infertility and reproductive problems in men. 	<ul style="list-style-type: none"> • Toxicity impacts in animals including damage to liver, kidney, lungs and reproductive systems.
Pharmaceuticals	Introduced through sewage from households with patients using drugs.	<ul style="list-style-type: none"> • Development of antibiotic-resistant strains of bacteria that can lead to a serious threat to human health. 	<ul style="list-style-type: none"> • Development of antibiotic-resistant strains of bacteria that can critically disturb natural bacterial ecosystems in the environment. • Under certain conditions direct impact on fish reproduction.
Personal Care Products	Health, beauty and cleaning products.		<ul style="list-style-type: none"> • Negative impact on aquatic ecosystems, especially related to endocrine disruption and reproductive disorders. • Create a layer on the water surface that hinders gaseous exchanges between the air and the sea.

Ref: Contaminants of Emerging Concern In The Mediterranean Sea, #40, April 2021, Planbleu; <https://planbleu.org/wp-content/uploads/2021/05/Pollution-emergentes-EN.pdf>

Problems with Designing the Treatment Removal Processes

- Emerging pollutants cannot be removed completely by the conventional water and wastewater treatment plants.
- No specific target compound – several compounds
- Hundreds of different structures and end groups
- EPs are present in low concentrations in large volumes of wastewaters
- EPs are present as multicomponent systems (mixtures of several EPs are present in a wastewater)

THEREFORE
Selecting/designing a single stage treatment system for an EP
wastewater source will not be sufficient

Pharmaceutical Residues in Municipal Wastewater

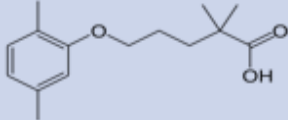
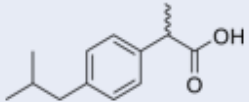
There are thousands of pharmaceuticals in use today. Some pharmaceuticals have been found in water and have raised concerns about the potential risks they pose to both humans and our ecosystems. These pharmaceuticals tend to make their way in to our waters primarily through excretion of active drugs directly from patients and subsequent incomplete removal of those pharmaceuticals from our wastewater during wastewater treatment. This webinar described our estimates of potential risks to people as well as aquatic life by combining aquatic concentration information with available dose-response data. This analysis includes data from our recent study of pharmaceutical concentrations in effluent samples from 50 very large municipal wastewater plants located across the United States. Contributors: Mitch Kostich, Angela Batt, Susan Glassmeyer, and Jim Lazorchak.

[Pharmaceutical Residues in Municipal Wastewater Webinar Supplemental Materials](#)

<https://www.epa.gov/water-research/pharmaceutical-residues-municipal-wastewater>

Case Study: Ibuprofen and Gemfibrozil Removal from TSE

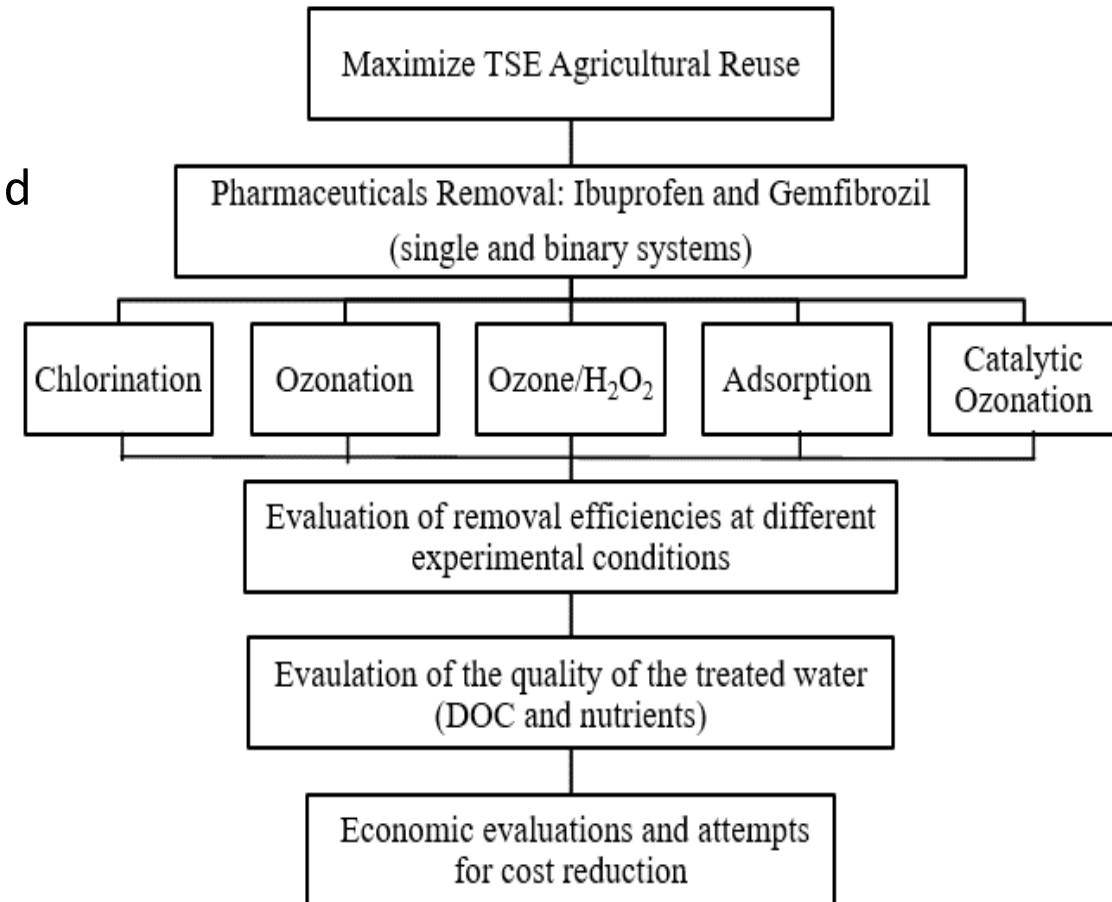
- Ibuprofen and gemfibrozil are persistent to the conventional wastewater treatment processes
- May enter the soil through irrigation with treated sewage effluent (TSE)
- Phytotoxic to plants such as carrots, tomatoes, and lettuce
- Cause feminization when exposed to male fish and reduction of egg fertilization, thus the fish population is reduced
- Affect human health through food chain

Compound	Group	Chemical Structure
Gemfibrozil	Lipid regulator	
Ibuprofen	Analgesic	



Case Study: Ibuprofen and Gemfibrozil Removal from TSE

- ❑ In this study, the removal efficiencies of ibuprofen and gemfibrozil were evaluated using several treatment technologies.
- ❑ Today's presentation will be focusing on:-
 - **Adsorption (date pits derived AC)**
 - **Ozone**
 - **Catalytic ozonation**



Case Study: Ibuprofen and Gemfibrozil Removal from TSE

Production of Activated Carbon

- ❑ Waste date pits were used as date palms are abundant in the region
- ❑ Grinded and impregnated with phosphoric acid at a mass ratio of 2:1
- ❑ Furnace temperature program under continuous nitrogen gas flow:
 - Started at room temperature with a ramp at 5 °C/min to 240 °C
 - Followed by a ramp at 2 °C/min to 360 °C
 - Then tamped at 5 °C/min to 550 °C and held for 2 hours
- ❑ The produced activated carbon was rinsed using filtration paper until the filtrate water pH was around neutral
- ❑ Grinded, and sieved to particle size of 75-125 μm



Case Study: Ibuprofen and Gemfibrozil Removal from TSE

Adsorption Performance

- ❑ The removal efficiency of both compounds was increased by increasing the activated carbon dosage.
- ❑ Gemfibrozil was completely removed after 48 hours of adsorption using 5 mg activated carbon. At higher dosages of 7 and 10 mg, complete removals were achieved within 24 hours.
- ❑ Ibuprofen was still detected after 72 hours where its removal efficiency was increased by increasing the activated carbon dosage from 1 mg to 10 mg with 33.73% and 88% removals, respectively.
- ❑ The enhanced adsorption by increasing the adsorbent dose is due to the increased number of available active sites for adsorption

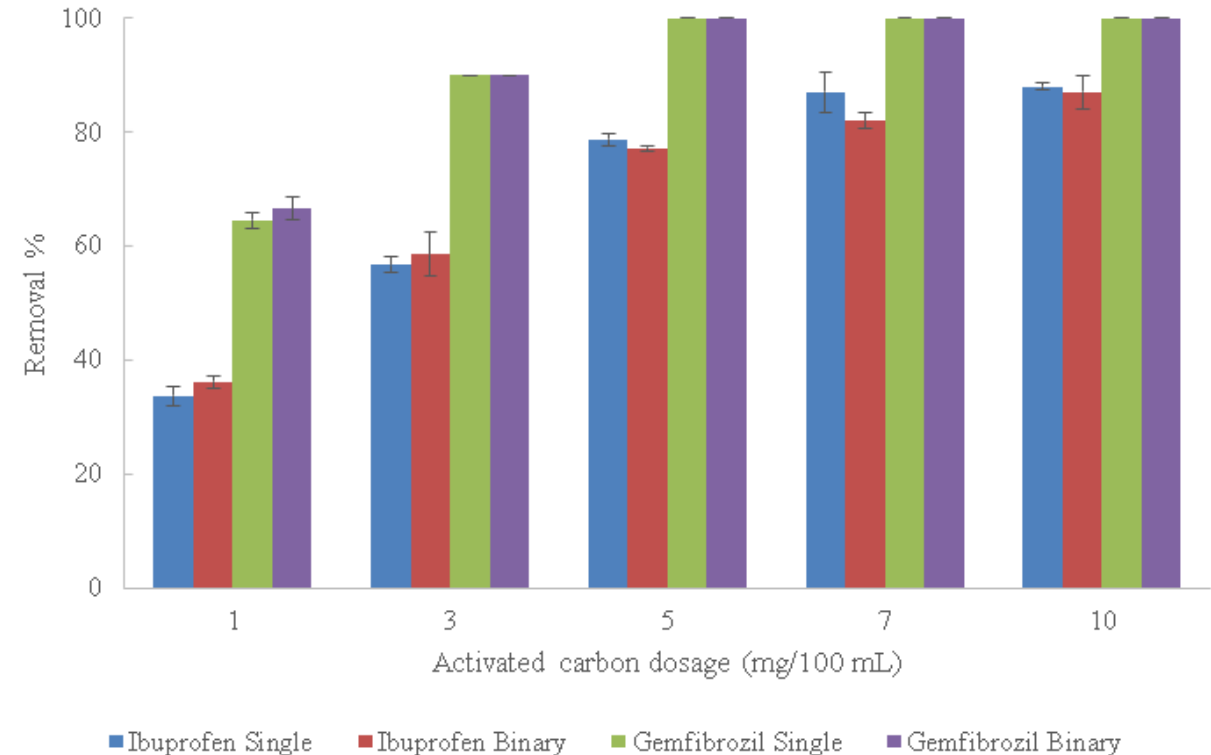
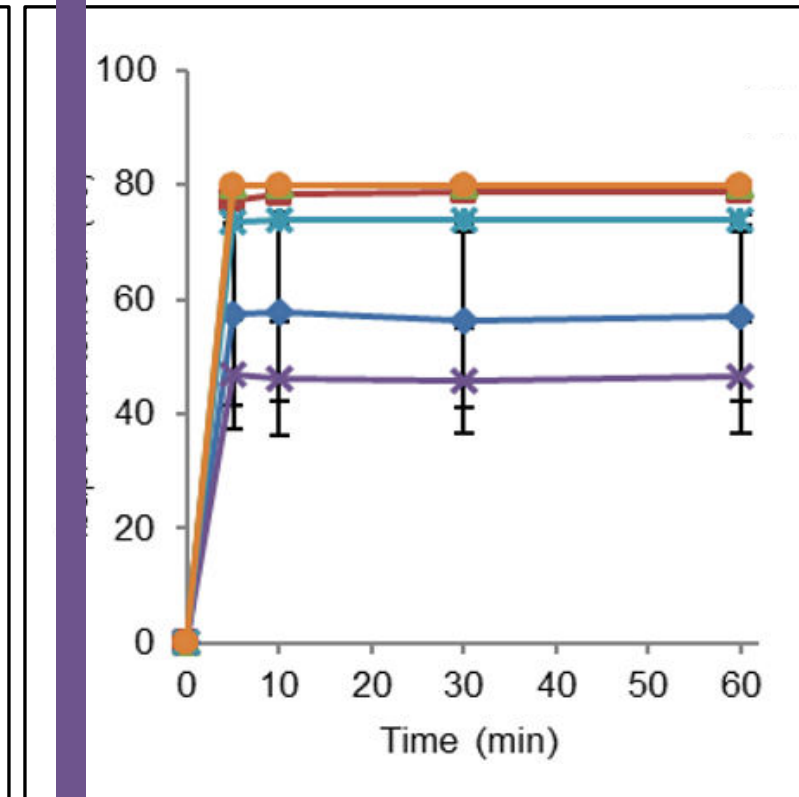
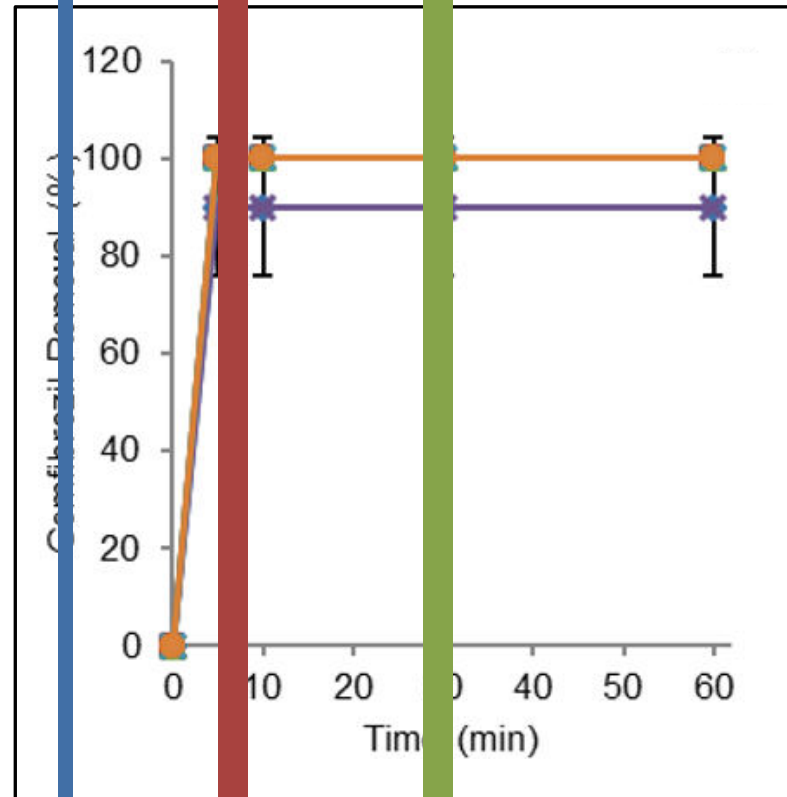


Figure 1: Effect of activated carbon dosage on the adsorption of ibuprofen and gemfibrozil from TSE after 72 hours of contact time. Initial ibuprofen conc. = 0.1 mg/L, initial gemfibrozil conc. = 0.1 mg/L, temperature = 20 °C, pH = 8.26, agitation speed = 200 rpm.

Case Study: Ibuprofen and Gemfibrozil Removal from TSE

Ozonation Performance

- ❑ Gemfibrozil: Complete removal was achieved at ozone dosages of 1 and 1.5 mg/L.
- ❑ Ibuprofen: At a dosage of 1 mg/L, 80% ibuprofen removal was achieved. An increase in the ozone dose to 1.5 mg/L did not show any further significant increase.
- ❑ Removal efficiency in the binary system is less than the single component test at the lower ozone dosage.

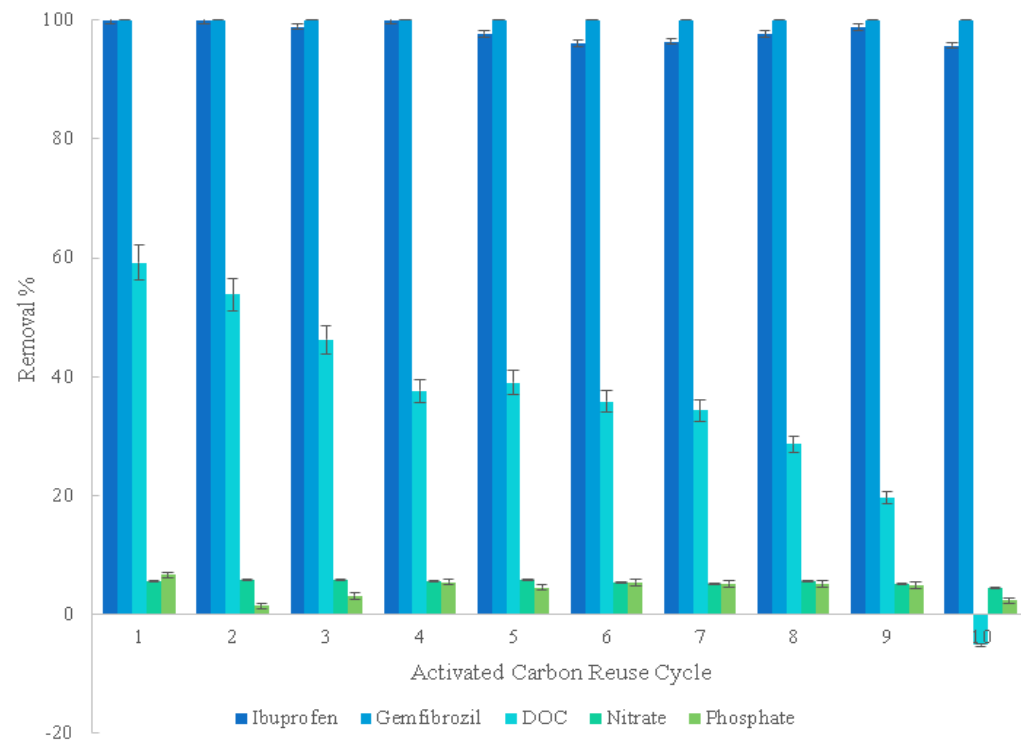


— 0.5 mg/L, — 1 mg/L, and — 1.5 mg/L in single component, — 0.5 mg/L, * 1 mg/L, and — 1.5 mg/L in binary systems

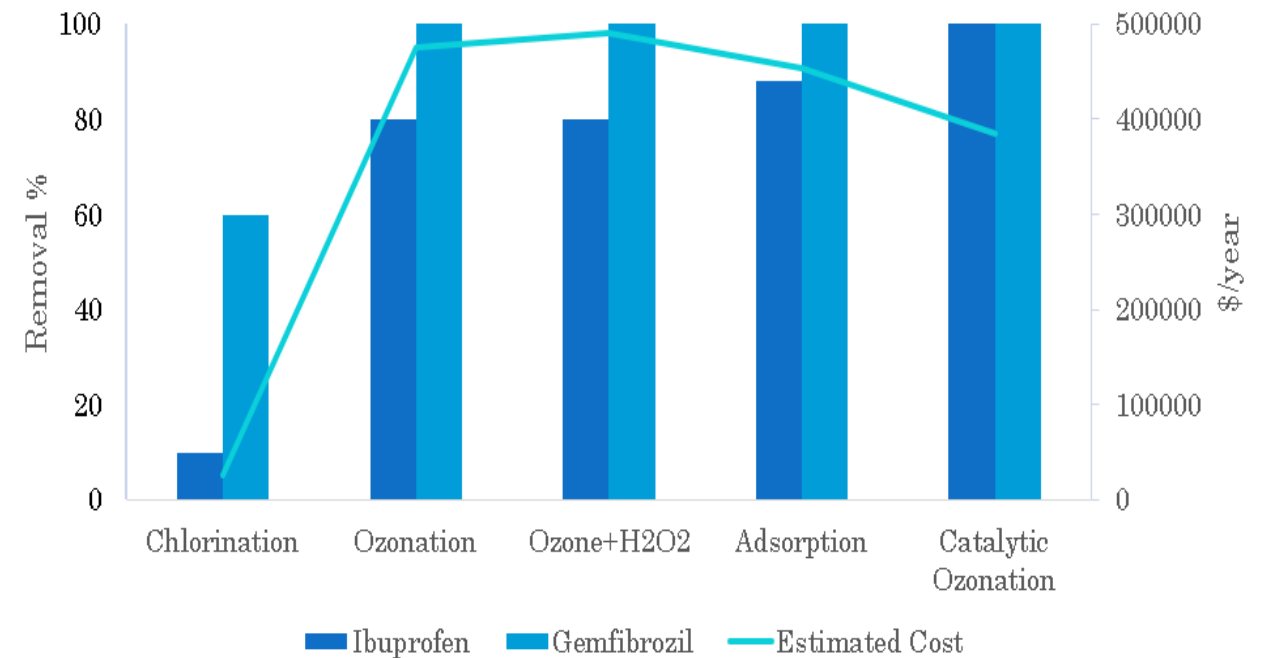
Case Study: Ibuprofen and Gemfibrozil Removal from TSE

Catalytic ozonation Performance

O₃ dose= 1 mg/L; AC dose= 10 mg/100 mL;
 Contact time= 4h



Cost Comparison



Conclusion and The way Forward

- ❑ High quality TSE is produced, suitable for agriculture reuse with low contaminants and high nutrients. The nutrients phosphate and nitrate concentrations were not affected.
- ❑ Although the cost of these tertiary treatment technologies are higher compared to the conventional treatment processes, however, these processes can significantly achieve higher removal efficiencies for different types of contaminants.
- ❑ Future work will include:-
 - Assessment of oxidation by-products
 - Assessment of bromate formation.
 - Pilot scale trial at local sewage treatment plant.