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Review article

Environmental concerns and bioaccumulation of psychiatric drugs in water bodies – Conventional versus biocatalytic systems of mitigation

Saúl Antonio Hernández Martínez [a], Elda M. Melchor-Martínez [a,b], Reyna Berenice González-González [a,b], Juan Eduardo Sosa-Hernández [a,b], Rafael G. Araújo [a,b], Jesús Alfredo Rodríguez-Hernández [a], Damià Barceló [c,d,e], Roberto Parra-Saldívar [a,b], Hafiz M.N. Iqbal [a,b,*]

[a] Tecnologico de Monterrey, School of Engineering and Sciences, Monterrey, 64849, Mexico
[b] Tecnologico de Monterrey, Institute of Advanced Materials for Sustainable Manufacturing, Monterrey, 64849, Mexico
[c] Department of Environmental Chemistry, Institute of Environmental Assessment and Water Research, IDEA-CSIC, Barcelona, Spain
[d] Catalan Institute for Water Research (ICRA-CERCA), Parc Cientific i Tecnològic de la Universitat de Girona, Edifici H_2O, Girona, Spain
[e] Sustainability Cluster, School of Engineering UPES, Dehradun, India

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ABSTRACT

The COVID-19 pandemic has brought increments in market sales and prescription of medicines commonly used to treat mental health disorders, such as depression, anxiety, stress, and related problems. The increasing use of these drugs, named psychiatric drugs, has led to their persistence in aquatic systems (bioaccumulation), since they are recalcitrant to conventional physical and chemical treatments typically used in wastewater treatment plants. An emerging environmental concern caused by the bioaccumulation of psychiatric drugs has been attributed to the potential ecological and toxicological risk that these medicines might have over human health, animals, and plants. Thus, by the application of biocatalysis-assisted techniques, it is possible to efficiently remove psychiatric drugs from water. Biocatalysis, is a widely employed and highly efficient process implemented in the biotransformation of a wide range of contaminants, since it has important differences in terms of catalytic behavior, compared to common treatment techniques, including photodegradation, Fenton, and thermal treatments, among others. Moreover, it is noticed the importance to monitor transformation products of degradation and biodegradation, since according to the applied removal technique, different toxic transformation products have been reported to appear after the application of physical and chemical procedures. In addition, this work deals with the discussion of differences existing between high- and low-income countries, according to their environmental regulations regarding waste management policies, especially waste of the drug industry.

1. Introduction

COVID-19 pandemic has affected the way that people used to live (lifestyle, hobbies, personal care, expenses, feeding, etc.) (van der Werf et al., 2021; Lee et al., 2020a,b), and how society relates professionally and casually (Sommerlad et al., 2021; Marra et al., 2020). In fact, during and after pandemic, important consequences in different areas have come, such as the economy crisis, which is mostly affected the mass unemployment (Kawohl and Nordt, 2020), government public debt caused by public health invest (Amis and Janz, 2020), lack of manufacturing, loss of service industries and weakening of global market (Pak et al., 2020); house violence (Bradbury-Jones and Isham, 2020), vulnerable education (Azorín, 2020) and mental health problems (Kumar and Nayar, 2021; Steardo and Verkhratsky, 2020), including depression and anxiety symptoms (Rabeea et al., 2021), bipolarity (Spelber and Strakowski, 2021), suicidal thoughts (Thompson et al., 2021), insomnia (Pappa et al., 2020), psychotic attacks (Janoczkin et al., 2021) and convulsions (Andraus et al., 2021).

As it is known, the COVID-19 pandemic led many countries to implement lockdowns and social distancing measures, including voluntary isolation and closure of schools, and restriction to non-essential activities . However, although these preventive measures are

* Corresponding author. Tecnologico de Monterrey, School of Engineering and Sciences, Monterrey, 64849, Mexico.
E-mail address: hafiz.iqbal@tec.mx (H.M.N. Iqbal).

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effective for the spread of COVID-19 (Tian et al., 2020), they have been reported to have an adverse effect on mental health (Galea et al., 2020). For example, it has been proven that different factors such as the number of deaths, mass unemployment, and isolation measures are the main causes of negative psychological effects on society (Galea et al., 2020), (Swami et al., 2021; Lee et al., 2020a,b; Thompson et al., 2021), and some other related problems, such as internet, the use of drugs, alcohol, and tobacco addictions (Marsden et al., 2020).

As a result, coronavirus-related stress, anxiety, and depression have increased the percentage of people seeking psychiatric treatment (Flament et al., 2021), leading to increased demand for psychiatric drugs, such as antidepressants, anti-anxiety drugs, mood stabilizers, and antipsychotics (Jacob et al., 2021). In fact, the increasing demand of this drugs has been confirmed by purchases studies made in Germany (Jacob et al., 2021; Kostev and Lauterbach, 2020), Italy (Ammassari et al., 2021), Canada (Stall et al., 2021), England (Howard et al., 2020), and United States (Vaduganathan et al., 2020). Thus, the widespread use and demand of these drugs, has raised environmental concerns, since the disposal of expired or unused drugs (approximately 50%) and the release of their metabolites from urine and feces introduces large amounts of these drugs into aquatic systems (Teymoorian et al., 2021). Moreover, different studies have shown that the bioaccumulation of these psychiatric substances may have negative effects on living organisms, such as endocrine disorders, and reproductive, growth and metabolic deficiencies (Argaluza et al., 2021; Thompson and Vijayan, 2020; Carter et al., 2018).

Due to the inability to remove psychiatric drugs from aquatic systems by wastewaters treatment plants (Escudero et al., 2021), different degradation and removal techniques have been studied and applied, such as photodegradation (Osawa et al., 2020), Fenton (Lumbaque et al., 2018), electrochemical procedures (Bosio et al., 2021), thermal degradation and some other combinations (Pinto et al., 2018; Mitsika et al., 2021). However, even though the application of these conventional techniques appears to be effective for the degradation/removal of psychiatric drugs, with some drugs achieving total degradation (Ferreira et al., 2018) by reviewing the most common detection techniques used after transformation reaction, it was observed that is common that many transformation products with adverse toxicological effects are formed (Lambropoulou et al., 2017). In the other hand, biocatalytic processes might have important advantages over traditional treatment methods, such as physical and chemical technologies, since they are environmentally friendly and a greener approach for removing these drugs from aquatic systems due to important characteristics such as high stability, simple operational processes, recyclability of catalysts, and a high bioconversion rate that results in less non-toxic transformation products (Sheldon and Woodley, 2018). Then, through this review, we discussed the use of biocatalytic systems as an alternative for the biodegradation of psychiatric drugs in aquatic systems, as well as the potential impacts of transformation products from degradation over living organisms; and the roll policies and regulations have in the development of highly quality wastewater treatment.

2. Environmental concern of psychiatric drugs

As mentioned, the overuse and the inability to completely remove psychiatric drugs from WWTPs has become in a recent environment concern. The overuse of psychiatric drugs might cause its released and increment of concentrations from different sources, including hospitals and houses to wastewater plants. (Nason et al., 2021). Hospitals indeed, produce a lot of medical wastes, including psychiatric drugs and transformation products released through feces and urine from patients but also through direct disposal of expired medicines (Pacheco et al., 2021), which in consequences lead to the bioaccumulation of this drugs in aquatic systems, including wastewaters, groundwaters, and surface waters. In fact, different studies have shown that these emerging contaminants are usually detected in aquatic systems in magnitude of concentrations of ng/to mg/L (Castillo-Zacarías et al., 2020), which in case of inadequate treatment, might cause a risk for both environment and public health (Pacheco et al., 2021).

2.1. Bioaccumulation of psychiatric drugs in aquatic systems

Pharmaceuticals are commonly one of the most detected emerging contaminants compounds in wastewater plants (Aydın et al., 2021). With the increasing demand and use of pharmaceuticals during COVID-19, wastewater samples influents and effluents have detected an increment in concentration of different pharmaceuticals, including COVID- 19 treating drugs, opioids, antibiotics, and psychiatric drugs (Nason et al., 2021). These last, appears to be the most recalcitrant group of drugs in wastewater treatment plants (WWTPs) (Aydın et al., 2021). In fact, different studies have shown how psychiatric drugs presents nearly the same concentration in influents than in effluent of the WWTPs. For example, a study made in a WWTPs in Medellin and Bogota, Colombia revealed how the concentrations of some non-psychiatric drugs like acetaminophen, ciprofloxacin, and norfloxacin, went from concentrations of 9.19 μg/L, 2.29 μg/L, and 1.37 μg/L in influent to concentrations of 0.16 μg/L, 0.81 μg/L, and 0.47 μg/L in effluent, respectively. On the other hand, psychiatric drugs, such as carbamazepine and venlafaxine presented concentrations of 0.153 μg/L, and 0.056 μg/L, in influent, and concentrations of 0.140 μg/L, and 0.035 in effluent, respectively, which means that non-psychiatric drugs had a removal percentage around 65–98% while psychiatric drugs removal percentage was around 8.5–35% (Botero-Coy et al., 2018).

Since the effluents from WWTPs are the higher source of psychiatric drugs release to aquatic systems due to inadequate removal for these compounds during traditional wastewater treatments (Dalecka et al., 2021), it is known that due to the bioaccumulation of pharmaceuticals, including psychiatric drugs, traces of drugs might move from aquatic systems and reach agriculture, drinking water, and natural habitats (Fig. 1) (Pacheco et al., 2021; Saadat et al., 2020).

The next sections are described of bioaccumulation of psychiatric drugs in different aquatic systems.

2.1.1. Wastewaters

Wastewaters are a complex mixture of solids, dissolved matter, microorganisms, heavy metals, and emerging contaminants, including psychiatric drugs (Warwick et al., 2013). Wastewater discharges are the inflexion point for the released of psychiatric drugs into other aquatic

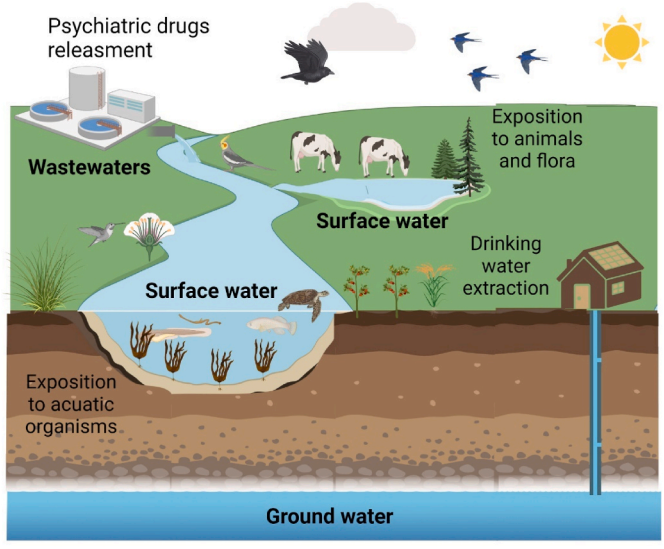

Fig. 1. Presence of psychiatric drugs in different aquatics systems and its contact with humans, flora, and fauna.

systems included in the cycle of water (Bijlsma et al., 2021). Indeed, a lot of studies have studied the presence of antidepressants in influents and effluents of WWTPs. For example, an analysis made with liquid chromatography couple with mass spectrometry (LC-MS) in four WWTPs in Belgium confirmed the presence in influents of about 18 of psychiatric drugs (e.g. sertraline, moclobemide and melitracen) in concentrations around of 25 ng/L (Boogaerts et al., 2019). Another study made in a municipal WWTPs in Canada conclude that primary and trickling filter/solids contact are not able to efficiently remove psychiatric drugs, such as venlafaxine (VFX) and its metabolite O-desmethylvenlafaxine (ODVFX), citalopram (CIT), and carbamazepine (CBZ), which were detected in concentrations up to 4.3 μg/L (Lajeunesse et al., 2012). Moreover, studies made in hospitals wastewaters have identified as one of the most common emerging contaminants presented in these wastewaters, psychiatric drugs, including CBZ, VFX, CIT, sertraline, diazepam, etc. (Nason et al., 2021; Teymoorian et al., 2021). Thus, monitoring and detection of psychiatric drugs before and after processing by wastewater plants become a major concern to reduce subsequent emissions to other aquatic systems.

2.1.2. Groundwaters

Since groundwaters represents almost 75% of fresh drinking water and it is widely implemented in agriculture, industry, and animal breeding, monitoring and detection of emerging contaminants in groundwater is important to make a proper quality assurance of the waters (Pinasseau et al., 2020). Different studies and techniques have been applied for the monitoring of psychiatric drugs in groundwaters. For example, an ultra-high liquid chromatography analysis made of groundwater samples one industrial community in Olomouc, Czech Republic, identified the presence of some antidepressants, antipsychotics, and transformation products at high concentrations (up to 1 mg/L) and it was concluded that further investigation in remediation was needed (Křesinová et al., 2016). Moreover, another study made across United States in almost 1100 sites, revealed that one psychiatric drug (carbamazepine) appears as one of the 4 most detected pharmaceuticals detected all the samples (Bexfield et al., 2019). Moreover, psychiatric drugs like carbamazepine, fluoxetine, and sertraline have been identified in concentrations up to 20 ng/L in different areas like cemeteries (Paíga and Delerue-Matos, 2016), urban communities (Wolf et al., 2012) and even rural communities (Chiffre et al., 2016). Contamination of groundwaters might be a high environmental concern due to it is the principal drinking water supply of many communities around the world, it is implemented in agriculture and animal husbandry, which means that can be directly in contact with humans through edible food primally.

2.1.3. Surface water

Surface waters, including sea, lakes, and rivers and streams represent another important aquatic system that has been detected to be compromised by the bioaccumulation of pharmaceuticals (psychiatric drugs included). Due to psychiatric drugs are more difficult to remove during WWTPs bioaccumulation in surface waters of these drugs has an increasing environmental concern (Dalecka et al., 2021). The presence of psychiatric drugs in surface waters has been extensively studied in different countries across Asia, Europe, and America (Jameel et al., 2020). For example, Bangladesh (Hossain et al., 2018), Sri Lanka and India (Guruge et al., 2019) studies that confirmed the presence of psychiatric drugs like carbamazepine at concentrations in the other of ng/L.

2.2. Toxicity of psychiatric drugs

Along the history, contamination of aquatic systems has provoked several consequences for microorganisms, food supplies, animals, and human being (Fig. 2). From bacterial and viral diseases (Pinon and Vialette, 2018) to radiation (Kryshev et al., 1998) or heavy metal (Fu and Xi, 2020) contaminate on. In case humans, the contamination of surface waters by psychiatric drugs becomes an important environmental concern since humans can be in direct contact with contaminated waters through swimming and recreational activities (Teymoorian et al., 2021), edible food contaminated for irrigation waters (Mordechay et al., 2021), catched fishes (Huerta et al., 2018) or even drinking water (Peng et al., 2019). For example, a study made in fishes collected in United States urban rivers commonly used for fishing, revealed that the psychiatric drugs carbamazepine and venlafaxine were the pharmaceuticals detected at higher concentrations (order of ng/L). A risk that human could present in case of be in constant contact with different psychiatric drugs, such as carbamazepine, phenothiazines and clozapine, is related to hematological toxicity that is presented by the combination of two or more drugs with neutropenia/agranulocytosis risk (Flanagan and Dunk, 2008). Moreover, recent studies have shown that antidepressant compounds in environmental concentrations, such as bupropion, negatively affect zebrafish in their early stages of life, demonstrating that psychiatric substances represent a possible risk to aquatic ecosystems and consequently human health (Franco et al., 2019).

Several studies have shown that even low levels of psychiatric drugs might affect the reproduction, growth and survivance of aquatic microorganisms and animals (Thompson and Vijayan, 2020). For example, samples of waters from a hospital WWTPs in Greece showed that the exposure to different psychiatric drugs, including bupropion, citalopram, fluvoxamine, sertraline and venlafaxine with algae, fishes and invertebrates resulted in high values of toxicity units according to risk quotient approach (RQ) (Papageorgiou et al., 2019). In addition, other studies also studied the toxicological effects of psychiatric drugs in aquatic systems, fluoxetine has been shown to alters fish behavior (Wiles et al., 2020), venlafaxine interfere with larval minnows' growth (Thompson and Vijayan, 2020), amitriptyline, fluoxetine and mianserin also affects the growth of zebrafish larvae (Wu et al., 2017), and

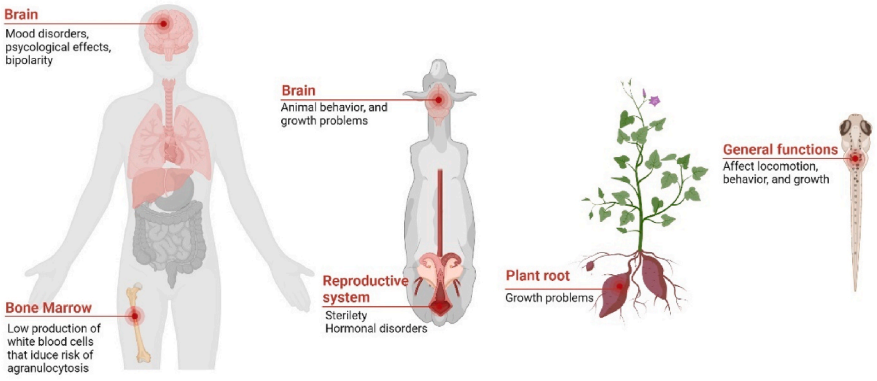

Fig. 2. Toxicological effects of psychiatric drugs in humans, animals, plants, and microorganisms (from the left to right, respectively.

carbamazepine and fluoxetine that affected the locomotion, DNA, and reproducibility of freshwater planarians (Ofoegbu et al., 2019). Moreover, the bioaccumulation of psychiatric drugs in organisms out of the aquatic systems is reported. For example, a study conducted by (Carter et al., 2018) reported that carbamazepine has inhibitory effects over the metabolism of plants.

Thus, the presence of psychiatric drugs in aquatic systems, including wastewaters, groundwaters and surface waters like rivers, streams, and lakes in different urban and rural communities across the world has been extensively studied. In general, results have concluded that psychiatric drugs are one of the most detected emerging contaminants in aquatic systems samples, in which drugs like carbamazepine and sertraline appears almost in all monitoring studies. This in consequence represents a highly environment concern due to its feasibility that reach aquatic organisms, plants, animals and even humans.

3. Conventional (non-biocatalytic systems) methods for psychiatric drugs removal in wastewater treatment

Wastewater treatment plants have the objective of removing pollutants from wastewater before reusing it or discharging it back to the environment. Typical wastewater treatment plants use diverse processes that are commonly divided into two treatment stages and some of them can include a tertiary treatment (Gerba and Pepper, 2019; Mandal et al., 2020; Singh et al., 2021a,b; Sonune and Ghate, 2004). Primary treatment involves physical processes for the removal of solids from wastewater (Mandal et al., 2020). Secondary treatment includes biological processes for the degradation of organic matter (Mandal et al., 2020; Sonune and Ghate, 2004). The tertiary treatment is stage where advanced treatments are conducted for removing the contaminants that could have not been removed during the first two stages (Dhodapkar and Gandhi, 2019; Gerba and Pepper, 2019). However, wastewater treatment plants usually have low removal efficiency of diverse persistent contaminants, including pharmaceuticals such as psychiatric drugs (Jelic et al., 2011; Wu et al., 2020; Zhang et al., 2008).

There are reports regarding the removal efficiency of diverse psychiatric drugs of wastewater treatment plants was evaluated. A research carried out by (Jelic et al., 2011) studied three different WWTPs during two years for evaluating the removal efficiency of 43 pharmaceuticals compounds, including psychiatric drugs such as carbamazepine, diazepam, and lorazepam. Samples of the influent, effluent, and the sludge were taken to determine the occurrence of the pharmaceuticals and the efficiency of the WWTPs. According to the results, 32 pharmaceuticals were detected at the influent, and after the treatment 29 were detected at the effluent, and 21 were accumulated in the sludge, which means the processes are moderately effective for removing psychiatric drugs.

As most of the current technologies of WWTPs do not have 100% of efficiency removing some specific contaminants such as psychiatric drugs, efforts have been made to develop or adapt technologies at lab-scale with potential as high-efficiency removal technologies. Different

Table 1
Degradation of psychiatric drugs by non-biocatalytic systems.

Method	Materials	Psychiatric drug	Degradation parameters	Time (h)	Removal/ degradation (%)	Ref
Photodegradation	ZnO, TiO_2	Amitriptyline[a,b,d]	1 mg/mL of ZnO and TiO_2, 25 °C, 0.03 mM of AMI, pH 6.7	1	55.3–94.3	Finčur et al., 2021
Photodegradation	TNW, Co-TNW, Fe-TNW, Ru-TNW	Trazodone[a]	20 mg of catalyst, 5 mg/L of TRA, 25 °C, pH 5.8–6.2	8	57–98	Osawa et al., 2020
Photodegradation	PLC	Clozapine[c]	300 mg/L of CZP, 50 ppm PLC, 30 °C,	2	94.2	Kumar et al., 2021
Photodegradation	Co-TNW	Amitriptyline[a,b,d], trazadone[a], venlafaxine[a]	10 mg/L of psychiatric drug, 10 mg of Co-TNW, pH 7, 25 °C	2	85–99	Osawa et al., 2019
Photo-Fenton	Iron (III) salt	Alprazolam[b], diazepam[b]	500 mL of psychiatric drug 10 mg/L, pH 2.9	2	~100	Mitsika et al., 2021
Fenton	Iron (II) salt	Diazepam[b]	500 μg/L of diazepam, 12.5–37.5 mg/L of Fe (II), 533 mg/L of H_2O_2, pH 5	1	~70–90	Lumbaque et al., 2018
Electro-Fenton	Iron plate anode, graphite rod cathode	Carbamazepine[b,d]	300 mL CBZ 5 mg/L, EF-Na_2MoO_4 electrolyte, pH 6.3, 0.145–0.580 mA/cm^2, 25 °C	1	80–85	Li, J. et al., 2021
Electron beam irradiation	Not apply	Fluoxetine[a]	50–100 mg/L of FLX, 0.5–5.0 kGy (irradiation dose), 20–22 °C	–	90–98	Shao et al., 2018
Electrochemical	Ti/Pt and BDD electrodes	Alprazolam[b], clonazepam[b], diazepam[b], lorazepam[b], carbamazepine[d]	25–75 A/m^2, 1 L reactor, 25 °C, 100 μg/L of psychiatric drug, pH 3–10,	60 min	40–99	Bosio et al., 2021
Ozonation	O_3	Citalopram[a]	2 mg/L of citalopram, 1.5 mg/L of ozone, pH 7, 25 °C	1 h	92	Nika et al., 2021
FO-EO	IrO_2-Ta_2O_5-SnO_2	Carbamazepine[b,d], Sulpiride[c]	10 mg/L of psychiatric drug, 20 °C, 480 min, 1 mA/cm^2, pH 5	480 min	86–89	Liu et al., 2018
Thermal degradation	Not apply	Citalopram[a], escitalopram oxalate[a]	1000 °C at increment of 10 °C/min, 15 mg of sample	20–45 min	27–74	Pinto et al., 2018
Thermal degradation	Not apply	Paroxetine[a], Sertraline[a]	1000 °C at increment of 5 °min, 7 mg of sample	28–58 min	~100	Ferreira et al., 2018
Advanced oxidation process	$CuFe_2O_4/MoS_2$, $2KHSO_5{\cdot}KHSO_4{\cdot}K_2SO_4$)	Fluoxetine[a]	80 mL of 20 mg/L of fluoxetine, 300 rpm, 1 M methanol, 1 M tert-butanol, 1.5 M ratio of catalyst, 20 min	20 min	97.7	Bai et al., (2020)
Adsorption	Fe_3O_4	Carbamazepine[b,d] Paroxetine[a] Lorazepam[b] Fluoxetine[a] Diazepam[b]	0.1 g of psychiatric drug, 1 g of adsorbent, pH 6.5	30 min	80–97	Aydın et al. (2021)
Adsorption	Biochar	Carbamazepine[b,d]	0.2 g of CBZ, 4–20 mg of adsorbent, pH 3-6	180 min	95	Naghdi et al., (2019)

[a] Antidepressant.
[b] Anxiolytic.
[c] Antipsychotic.
[d] Mood stabilizer, Amitriptyline (AMI), Carbamazepine (CBZ), Trazodone (TRA), Fluoxetine (FLX).

methodologies for the removal of psychiatric drugs have been reported, in general it can be classified as psychical or chemical techniques (Table 1), including adsorption (Rasheed et al., 2020), membrane filtration (Rizzo et al., 2019), photodegradation (Osawa et al., 2020), Fenton process (Lumbaque et al., 2018), electrochemical degradation (Bosio et al., 2021), and some others.

3.1. Physical treatments

Physical treatments reported for removing psychiatric drugs from water include adsorption, membrane filtration, and thermal degradation (Graumans et al., 2021; Rasheed et al., 2020; Rizzo et al., 2019). Adsorption is promising approach for removing contaminants, as there is a wide range of adsorbents, it is a straightforward process with lower operation costs compared to technologies such as reverse osmosis (Crini and Lichtfouse, 2019). There are reports of several adsorbents, such as activated carbon, biochar, and metal oxide nanoparticles, that were successfully employed for removing diverse psychiatric drugs (Rizzo et al., 2019; Rocha et al., 2020). For example, a study carried out by (Aydın et al., 2021) employed magnetite (Fe_3O_4) red mud nanoparticles (RM-NPs) for the adsorption of carbamazepine, paroxetine, lorazepam, fluoxetine, and diazepam. The results showed a removal efficiency between 80% for lorazepam and 97% for diazepam from the initial concentration of 0.1 mg/L within 30 min. Moreover, biochars and activated carbon have been applied for the adsorption of carbamazepine from wastewaters, in which it was possible to remove concentrations ranging from 0.5 to 20 ppb (Naghdi et al., 2019; Pereira et al., 2021).

Another example of psychical treatment is membrane filtration (e.g., forward osmosis). The main advantages of this technology include that no chemicals are needed, low solid waste generation and high efficiency (Crini and Lichtfouse, 2019; Meshksar et al., 2020). This methodologically approach have showed better results for the degradation of psychiatric drugs compared to simple adsorption techniques (Naddeo et al., 2020). For example, (Liu et al., 2018), evaluated the removal of carbamazepine and sulpiride, by coupling a forward osmosis membrane (FO) with electrochemical oxidation (EO) and obtain degradation efficiencies greater than 94%.

Membrane filtration is another common contaminant removal technology for removing contaminants from water. The main advantages of this technology include that no chemicals are needed, low solid waste generation and high efficiency (Crini and Lichtfouse, 2019). The material of the membrane, ceramic or polymeric, and the pore size are the main characteristics that influence the application and efficiency of membrane filtration (Meshksar et al., 2020).

In contrast, even though thermal treatment of water has been reported in the literature for the removal of contaminants from water, and desalination (Akay et al., 2021; Graumans et al., 2021; Hao et al., 2022; Pang et al., 2020), it is required to conduct more studies regarding the application of thermal treatments in the degradation of psychiatric drugs from water, as the publications related to thermal degradation of psychiatric drugs are focused on the thermal approach but not in aqueous media (Ferreira et al., 2018; Pinto et al., 2018).

Physical treatments such as membrane filtration or adsorption are very employed in psychiatric drugs removal as they offer some advantages, for example most of them do not require harmful chemicals, nor produce toxic reaction transformation products. However, they also have some drawbacks, as it is required and additional step for degrading or confining the contaminant removed from water. I this way, further research is needed to develop cheaper materials with higher selectivity to enable the application of these technologies at real conditions in a WWTPs. Also, it is required to conduct more studies where combined processes are employed, for example UV degradation/filtration, as a possible alternative for degrading the concentrated contaminants.

3.2. Chemical treatments

Chemical treatments are widely employed in water decontamination of a wide range of chemicals from water, as compared to other technologies the contaminants are degraded into non-toxic compounds and in most cases, it is not required further steps (Ahmed et al., 2017). For the degradation of psychiatric drugs, among the most employed technologies are photodegradation (Trawiński and Skibiński, 2017), electrochemical (García-Espinoza et al., 2018), and advanced oxidation (Saeid et al., 2020), like Fenton process (Oller and Malato, 2021) or ozonation (Nika et al., 2021).

Photodegradation is a technology that uses UV radiation or visible light as source of energy for breaking down the molecules of contaminants present in water and transforming them into other less harmful compounds in most cases (Blánquez et al., 2020). This technology has been applied for the degradation of psychiatric drugs such as carbamazepine (Baena-Nogueras et al., 2017), alprazolam (Shi et al., 2019), benzodiazepines (Calisto et al., 2011), among others. A research conducted by (Osawa et al., 2019), evaluated the photodegradation of venlafaxine, trazodone, amitriptyline using UV–Vis radiation and nanowires of cobalt-titanate as photocatalyst (Co-TNW). The results showed that the use of the photocatalyst enhanced the removal efficiency of amitriptyline compared to the photolysis without the catalyst. For trazodone, a removal of 90% was achieved after 15 min. For the venlafaxine a removal efficiency of 99% was achieved after 90 min in both cases, with catalyst and without using it. Moreover, the photodegradation under simulated solar light radiation of carbamazepine using a $BiOCl/Fe_3O_4$ composite as catalyst was evaluated in a study by (Chen et al., 2017). They reported that the efficiency of the degradation of carbamazepine was 90.3% after 60 min. Also, the effect of anions in water during the degradation was evaluated, showing that nitrate slightly increased the photodegradation, while the inhibiting effect was in the order of $CO_3^{2-} > SO_4^{2-} > Cl^-$.

Advanced oxidation processes (AOP) are a group of chemical treatments where the contaminants in water are oxidized through the reaction with hydroxyl radicals into safer or easier to handle compounds (Dave and Das, 2021). Some of the most reported AOPs include ozonation, Fenton processes, and electrochemical oxidation. In the ozonation, ozone (O_3) is using as oxidant due to its highly oxidizing capability. Researchers reported the use of ozonation assisted by UV radiation for the degradation of carbamazepine in wastewater (Somathilake et al., 2017). The authors evaluated the dosage of O_3, the wavelength and intensity of radiation. The results showed that using a dose of 14.4 mg/h a degradation below the detection limits was achieved after 0.5 min. The intensities of UV radiation with better results were 0.62 mW/cm^2 for UVA and 0.82 mW/cm^2 for UVC. Moreover, A research conducted by (Aghaeinejad-Meybodi et al., 2021), studied the ozonation and catalytic ozonation of fluoxetine comparing the efficiency in the presence of boehmite and γ-alumina as catalysts. Results demonstrated that pH had a major influence on the efficiency of the process, as the removal was less than 50% at pH of 7 but increased as with higher pH.

Fenton processes or Fenton reaction consists in the oxidation by strong oxidizing agents, such as hydroxyl, produced by the catalytic decomposition of hydrogen peroxide by Fe^{2+} and/or Fe^{3+} (Vasquez-Medrano et al., 2018). There are variations of the traditional Fenton process, like photo-fenton, that additionally combines the use of UV and/or visible light, increasing the ratio of degradation of contaminants (Ameta et al., 2018). Electro-Fenton is another variation that is reported for the degradation of psychiatric drugs and other contaminants, which consists in the Fenton's reaction taking place in an electrochemical cell (Gümüş and Akbal, 2016).

A study carried out by (Dwivedi et al., 2016) evaluated a Fenton process coupled with ozonation for the degradation of carbamazepine and oxcarbazepine in simulated wastewater. The authors used Response Surface Methodology to find the optimal conditions for the degradation of the psychiatric drugs, and reported that at pH 2, a Fenton dosage of

1.61 g/dm^3, 0.427 of Fe^{2+}/H_2O_2 ratio the degradation was 92.49% after 25 min. Additional study conducted by (Mitsika et al., 2021) evaluated photo-Fenton degradation of alprazolam and diazepam and optimized the process. The authors reported that the Response Surface Methodology allowed the optimization of the parameters, and the degradation efficiency of alprazolam and diazepam was 100% after 180 min.

Electro-Fenton processes were evaluated in the degradation of carbamazepine from water without using any extra oxidant in a study conducted by (Li, J. et al., 2021). The system did not use H_2O_2 and the reaction took place in the presence of sodium molybdate. After 60 min the removal efficiency was near to 100%, compared to traditional electro-Fenton which only achieved 34%. Also, electrochemical oxidation has been evaluated in the degradation and detection of psychiatric drugs in water. This process consists in the either by direct oxidation of the drugs by the electron transfer from the contaminant to the anode, or indirect oxidation through the generation of oxidizing species like hydroxyl radicals (da Silva et al., 2021).

A study evaluated the electrochemical oxidation of alprazolam, clonazepam, diazepam, lorazepam, and carbamazepine from water using as electrodes platinum-coated titanium and boron-doped diamond (Bosio et al., 2021). The authors evaluated different current densities, pH, and electrolyte concentrations. The results showed that all the drugs were degraded after 5 min at a current density of 75 A/m^2 for both electrodes. The effect of matrix was evaluated using municipal wastewater, and the degradation efficiency was 40% for platinum coated titanium and 33–52% for boron-doped diamond.

4. Biocatalytic systems to remove psychiatric drugs from wastewaters

Biocatalysis is the result of the advances in molecular biology and biotechnology achieved during the past two decades (Sheldon and Woodley, 2018), which appeared as result of the necessity to develop greener, sustainable, and profitable processes in different industries, including pharmaceutical industry (Bell et al., 2021), food industry (Bilal and Iqbal, 2020), fine chemicals production industry (Thompson et al., 2018), and more recently, in bioenergy production processes (Kim et al., 2018). The increasing interest in biocatalysis is since it provides significant benefits over conventional catalysis (e.g., inorganic catalysts), such as higher catalytic properties, high specificity, high reaction rate under mild reaction conditions of pH and temperature, low energy consumption, and biodegradability (de Jesús Rostro-Alanis et al., 2016), which are primarily given by two fundamental principles: (1) biocatalysts are not consumed or permanently modified during catalysis reactions, and (2) chemical equilibrium is not altered by the presence of biocatalysts (Lopez-Cantu et al., 2022).

Moreover, biocatalysis processes have been widely applied for the biodegradation/biotransformation of a wide range of emerging contaminants, such as personal care products, industrial chemicals, steroids hormones, pesticides, and pharmaceuticals, in which are included psychiatric drugs (Asif et al., 2018). In general, the bioconversion of psychiatric drugs by biocatalytic systems have been achieved in three different ways (Fig. 3): (a) whole-cell biocatalysis, (b) isolated-enzyme biocatalysis, and (c) isolated-immobilized enzyme into a nanomaterial (Bilal and Iqbal, 2019; Sheldon and Woodley, 2018, Martínez et al., 2022).

4.1. Whole-cell biocatalysis of psychiatric drugs

The whole-cell biocatalytic process, which is represented in Fig. 4a, represents those cases in which the growth of the biocatalyst and the subsequent catalytic reaction occurs all in a whole-cell format (Sheldon and Woodley, 2018). This format of biotransformation has been used in different biotransformation processes due to several advantages, such as high surface-area-to-volume ratio, high catalytic activity, and low energy requirements (Pinto et al., 2020; Liu et al., 2019). However, the whole-cell biocatalysis approach presents some disadvantages related to the low diffusion rate of the substrate into the cell to the reaction centers, where takes place the enzymatic reaction (Kladko et al., 2020), which leads to low stability, cross reactivity, impossibility to recycle the

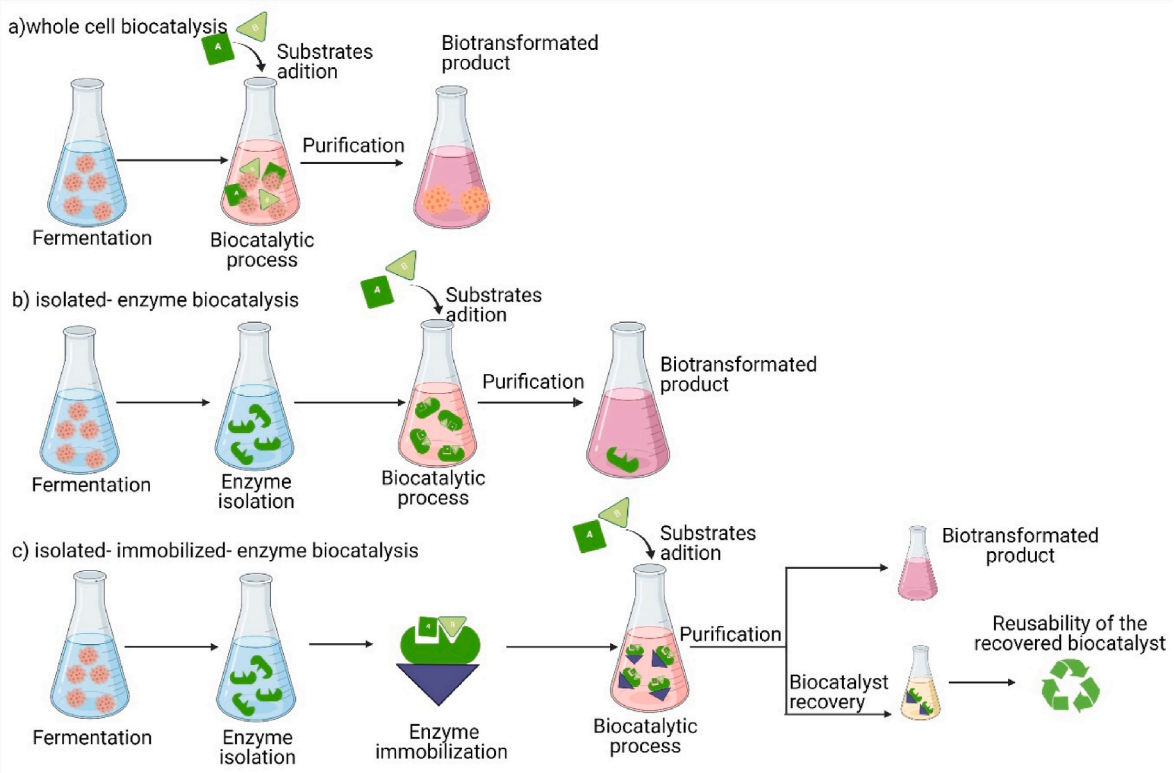

Fig. 3. Schematic illustration of various routes to design and deploy biocatalytic processes. Reprinted from Martínez et al., 2022 with permission from Elsevier.

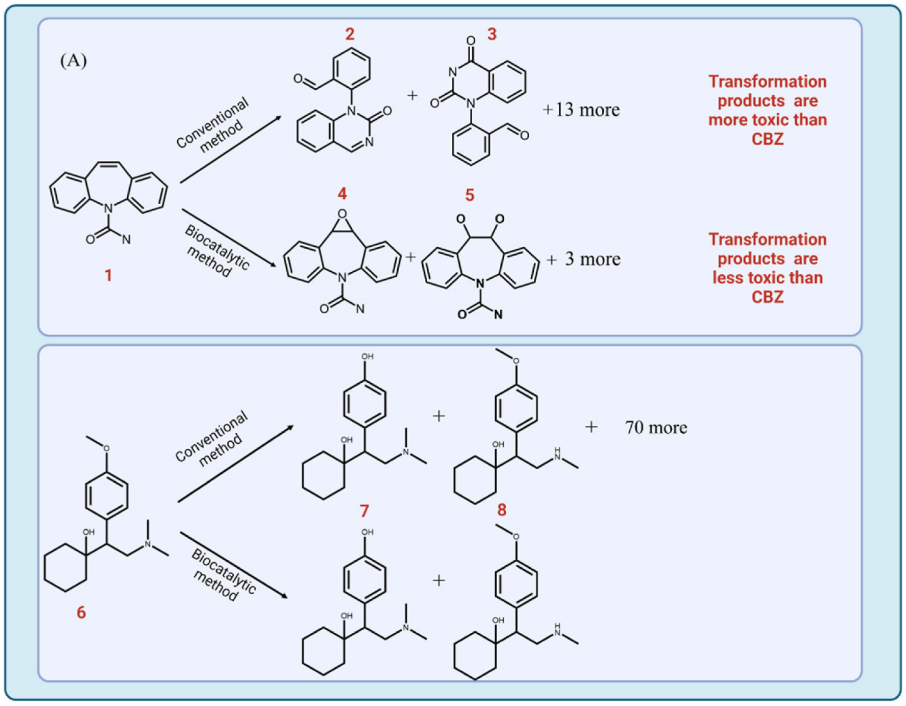

Fig. 4. Principal transformation products formed by conventional and biocatalytic treatments of (a) carbamazepine, and (b) venlafaxine. (1: CBZ,2: BQM, 3: BQD, 4: CBZE, 5: CBZD, 6: VFX, 7: ODMVFX, 8: NDMVFX).

biocatalyst and time-consuming purification steps (Sheldon and Woodley, 2018; Haghighatian et al., 2020).

Different psychiatric drugs have been successfully biotransformed by whole-cell biocatalysis (Table 2). For example, Kózka et al. removed some common antidepressants, such as sertraline, clomipramine, mianserin and paroxetine using a white-rot fungus *Pleurotus ostreatus* (Kózka et al., 2020). Results show that it was possible to biodegrade 96% of some antidepressants in 96 h. Another study conducted by (Llorca

Table 2
Biocatalysis of psychiatric drugs by whole cell biocatalysis.

Biologic agent	Source	Psychiatric drug	Type of sample solution	Time (h)	Remove conditions	Removal/ Degradation (%)	Reference
Pleurotus ostreatus	White-rot fungus from Manassas Virginia	Sertraline[a], Clomipramine[a], mianserin[a], paroxetine[1]	Psychiatric drugs mixture in ultrapure water	4–96	26 °C, 110 rev/min, 2.5 μg/mL and 100 mg/mL of sample	20–96	Kózka et al., (2020)
Trametes versicolor and G. lucidum	Commercial	Venlafaxine[a], O-desmethylvenlafaxine[a]	Ultrapure water	360	2 mg/L of VFX and ODVFX, sterile media, pH 4.5, 25 °C	70–100	Llorca et al., (2019)
Stropharia rugosoannulata, Ganoderma lucidum,	Donated by University of Helsinki	Venlafaxine[a], carbamazepine[b,c]	Stock solution with psychiatric drugs	144	25 °C, 135 rev/ min,100 mL of medium, 4.5 g/L of cultive pellets, 40–184.7 μg/mL of sample, dark conditions	70–75%	Castellet-Rovira et al., (2018)
Trametes versicolor, Aspergillus luchuensis	*Trametes versicolor* native from Brunswick, Germany and *A. luchuensis* native from Stockholm, Sweden	Carbamazepine[b,c]	Wastewaters	168	50 g of biomass, 25 °C, 120 rev/min	<30	Dalecka et al., (2021)
Chlorella sorokiniana, Chlorella vulgaris, Chlorella saccharophila, Coelastrella sp., *Coelastrum astroideum, Desmodesmus* sp., *Scenedesmus* sp., *Scenedesmus obliquus*	Northern Sweden green algea	Amitriptyline[a], carbamazepine[b,c], oxazepam[b]	Psychiatric drugs mixture in ultrapure water	288	25 °C, 120 rev/min, 100 mg/L of biomass, pH 7.2, 1 μg/mL of psychiatric drug	24–92	Gojkovic et al., 2019

3Antipsychotic.
[a] Antidepressant.
[b] Anxiolytic.
[c] Mood stabilizer, Venlafaxine (VFX), O-desmethyl venlafaxine (ODVFX), fluoxetine (FLX).

et al., 2019) was able to completely remove venlafaxine its metabolite desmethylvenlafaxine using commercial *Trametes versicolor* and *Ganoderma. lucidum* within 360 h.

Even though whole-cell biocatalysis is the simplest way to apply biocatalysis for the biotransformation of psychiatric drugs, it seems to have as greater disadvantage the total time that takes to degrade and purified the products. In addition, the biotransformation of some other mood stabilizers and anxiolytics, such as amitriptyline, carbamazepine and oxazepam, has been successfully achieved in a time rage between 144 and 360 h by the application of different microorganisms, including *Chlorella sorokiniana* (Gojkovic et al., 2019), *Aspergillus luchuensis* (Dalecka et al., 2021) and *Stropharia rugosoannulata* Castellet-Rovira et al. (2018).

4.2. Isolated-enzyme biocatalysis of psychiatric drugs

The isolated-enzyme biocatalysis process is represented in Fig. 4b. It consists in the application of purified enzymes extracted from cells with the principal objective to overcome the diffusional limitations that occurs in the whole-cell biocatalysis (Sheldon and Woodley, 2018). The isolated-enzyme biocatalysis is based in the principle that enzymes are natural biocatalysts that can be implemented to catalyze chemical reactions without affecting the chemical equilibrium of the reaction media (de Jesús Rostro-Alanis et al., 2016). Therefore, this biocatalytic approach provides selectivity for the efficient biotransformation of a wide range of water pollutants, such as dyes (Routoula and Patwardhan, 2020), plastics (Magalhães et al., 2021), and pharmaceuticals (Asif et al., 2018), including psychiatric drugs.

Even though there are different enzyme that have been applied for the biotransformation of psychiatric drugs, such as horseradish peroxidase, lignin peroxidase and soybean peroxidase (Pylypchuk et al., 2020; Morsi et al., 2021), laccases are the most common enzymes implemented for the degradation of psychiatric drugs due to its important characteristics. Laccases are multi-copper extracellular enzymes obtained from fungi, plants, insects, and a few bacteria (Masjoudi et al., 2021). The widespread application of laccase enzymes is due to the ability to catalyze the oxidation of a variety of organic substrates without the presence of oxidizing agents (Lopez-Cantu et al., 2022).

Commercial laccases and laccases from different microorganisms, such as *Trametes versicolor* (Asif et al., 2018), *Aspergillus oryzae* (Tufail et al., 2021), and *Paraconiothyrium variabile* (Ostadhadi-Dehkordi et al., 2012) have been applied for the biotransformation of psychiatric drugs (Table 3). For example, the anxiolytic and mood stabilizer, carbamazepine was biotransformed by commercial laccases using ABTS as mediator to reach 95% of degradation within 24 h (Naghdi et al., 2018). Moreover, compared to whole-cell biocatalysis, the isolated-enzyme assisted biocatalysis have shown that biotransformation can be achieved in shorter times, since a wide range of psychiatric drugs have been successfully degraded using laccases in a time range between 1 h and 72 h, which is shorter than the range in whole-cell biocatalysis (Alharbi et al., 2019; Gonzalez-Gil et al., 2019; Tufail et al., 2021).

However, this biocatalytic approach presents some disadvantages, including that lower biotransformation rates are achieved due to their lack of long-term operational stabilities (Xie and Zang, 2018). For example, a study conducted by (Gonzalez-Gil et al., 2019) implemented a mixture of different enzymes, including laccases, revealed that the anxiolytic venlafaxine was degraded only around 50% within 72 h, which is the longest time reported in enzyme catalyzed biodegradation. Moreover, the cost of using free enzyme is such that reuse is necessary, however, isolated enzymes are hardly recyclable and separable (Masjoudi et al., 2021).

4.3. Isolated-immobilized enzyme biocatalysis of psychiatric drugs

In Fig. 4c, it is schematically represented the implementation of isolated-immobilized enzymes in a biocatalytic process. The

Table 3
Biocatalysis of psychiatric drugs by isolated enzymes.

Enzyme	Source	Psychiatric drug	Type of sample solution	Time (h)	Remove conditions	Removal/ Degradation (%)	Reference
Laccases	(ATCC (American Type Culture Collection) 20869)	Carbamazepine[b c]	Ultrapure water	24	35 °C, pH 6, 60 U/L of enzyme concentration and 18 μM of ABTS	95	Naghdi et al., (2018)
Laccases	*Aspergillus oryzae*	Amitriptyline[a], carbamazepine[b c],	Synthetic wastewater containing a mixture of organic trace materials	24	20 μg/L of sample, 100 μg/min of enzyme, 30 °C	60–99	Asif et al., (2018)
Laccases	*Trametes versicolor*	Carmazepine[b c],	Ultrapure water	48	1.25–5.00 mg/L of CBZ, enzyme activity of 430–460 U/L, 25 °C, pH 6.9	82	Alharbi et al., (2019)
Laccases	Commercial laccases from *Aspergillus oryzae*	Carbamazepine[b c]	Ultrapure water	1	1 mg/L of CBZ, 95–100 μM/min of laccase, 30 °C	70	Tufail et al., (2021)
Laccases	Soil ascomycete, *Paraconiothyrium* variabile	nitrazepam, alprazolam, diazepam, oxazepam, clobazam, chlordiazepoxide, lorazepam	Ultrapure water	48	10 μg/mL of sample, enzyme activity 20 U/mL, 2 mM of HBT mediator, 35 °C	4.7–88.1	Ostadhadi-Dehkordi et al., (2012)
Mixture of enzymes	Anaerobic sludge	Venlafaxine[b]	Ultrapure water	72	0.1 ng/μL of sample, 100 μL of enzymes, anaerobic atmosphere, 30 °C	~50	Gonzalez-Gil et al. 2019

[3]Antipsychotic.
[a] Antidepressant.
[b] Anxiolytic.
[c] Mood stabilizer, Carbamazepine (CBZ),2,2′-Azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS), 1-hydroxybenzotriazole (HBT).

immobilization of enzymes consists in convert the enzyme from its homogenous form to a heterogenous catalysts by the addition of solid supports in which the enzyme is tagged using different immobilization methods, such as adsorption, covalent binding, cross-linking, entrapment, and encapsulation (Morsi et al., 2021). By the immobilization of enzymes into solids supports it is possible to overcome the major disadvantages of using free enzymes in biocatalytic processes due to it increment the long-term stability of the enzymes, providing resistant to degradation or denaturation (Bilal and Iqbal, 2019). Moreover, the addition of solid supports in the biocatalyst design facilitates the separation of the biocatalyst from the product stream and, thereby, it allows recycling (Sheldon and Woodley, 2018).

The design of nanobiocatalysts for the biodegradation have been reported for the degradation of psychiatric drugs (Table 4). Following the tendency of the isolated-enzyme biocatalysis, laccases are the most common enzymes used in immobilized form to biodegrade these compounds. Different nanomaterials are reported for the immobilization of laccases to remove psychiatric drugs from waters, including polymers (Simón-Herrero et al., 2019), metals and metal oxides (Guardado et al., 2021), and carbon-based materials (Masjoudi et al., 2021). For example, polyamide aerogels were implemented to covalently immobilize laccases from *Trametes versicolor* and catalyze the biotransformation of carbamazepine (Simón-Herrero et al., 2019). The biodegradation assays conducted to conclude that this nanobiocatalyst was able to remove 76% of the psychiatric drug within 24 h. Also, this nanobiocatalyst presented excellent reusability properties since it retained 22% of its initial activity after seven cycles of use. Moreover, a study made by (Naghdi et al., 2017), demonstrated that adsorption is other immobilization technique that can be implemented to remove anxiolytics from secondary effluent of wastewaters. In this study, a nanobiocatalyst was design by adsorbing laccases into nanobiochar structure, which allowed to remove 86% of carbamazepine within 24 h during 3 continuous cycles.

In addition, some other enzymes have been applied for the biotransformation of psychiatric drugs. For example (Pylypchuk et al., 2020), completely degrade carbamazepine using peroxidases immobilized in a core-shell composite of magnetite and silica (Fe_3O_4@SiO_2). The encapsulated enzymes showed promising recycle properties since 50% of the initial activity was retained after 20 cycles of use.

Recycling will depend primarily on the type of material and immobilization method (Bilal et al., 2018). In this term, not every nanobiocatalyst will be capable to be reused many times as other ones, for example, a soybean peroxidase immobilized covalently into zinc oxide retained 95% of initial activity after 4 cycles (Morsi et al., 2021), whereas a laccase nanobiocatalyst designed with the covalently immobilization into silica nanoparticles retain almost 28% of its initial activity but after 7 cycles.

4.4. Comparison of conventional versus biocatalytic systems

As it has been discussed in this review, conventional degradation techniques, including physical and chemical treatments; and biocatalytic processes might have both advantages and disadvantages. For example, it has been demonstrated that conventional methods such as photodegradation might remove completely psychiatric drugs from wastewater (Osawa et al., 2019). In general, both physical and chemical treatments have been widely implemented for the degradation process due to the high rates of removal that are usually obtained. However, even though these degradation approaches are efficient for the degradation of psychiatric drugs, high energy consumption is needed (Haghighatian et al., 2020). Moreover, due to typically chemicals and special materials are needed to implement these technologies, it has been reported that many undesired products can be produced (Liu et al., 2019). For example, it was reported that after the photodegradation of venlafaxine from water, almost 70 transformation products were formed (Lambropoulou et al., 2017). In comparison to biotransformation process (Gonzalez-Gil et al., 2019), also reported the removal of venlafaxine from waters, however, there wasn't by-product detection.

Moreover, biotransformation is characterized by its non-toxic and biodegradable behavior, which in comparison to non-biocatalytic technologies, biocatalysis appears as green and sustainable approach that follows almost the 12 principles of green chemistry (Haghighatian et al., 2020; Sheldon and Woodley, 2018). Thus, biocatalysis can be considered as a more efficient approach to remove psychiatric drugs from aquatic systems.

5. Transformation products of psychiatric drugs and their detection/monitoring

Techniques such as ozonation and UV photolysis have shown excellent performance on the removal of psychiatric drugs (Ikehata et al., 2006; Naghdi et al., 2018); however, complete oxidation and mineralization are typically not achievable, thus, releasing transformation products (TPs) (Donner et al., 2013; Naghdi et al., 2018). Historically, research efforts on environmental monitoring of pharmaceutical residues have been focused on the parent compounds (Boix et al., 2016; Li et al., 2022; Wang et al., 2021; Yang and Carlson, 2004). However, the persistence and ecotoxicological effects of TPs,occasionally with higher toxicity than parent compounds have led to an increased research interest in their detection (Boix et al., 2016; Ferrer and Thurman, 2012; Singh et al., 2021a,b) and with it, the urgent need for powerful analytical methods since their detection/identification is challenging due to complex degradation mechanisms and because there are no analytical standards for most of TPs (Huntscha et al., 2012; Osawa et al., 2019).

Nevertheless, advances in environmental analysis by mass spectrometry technologies had enabled rapid, selective, and robust quantification of TPs and the detection of unknown compounds (Haddad and Kümmerer, 2014; Osawa et al., 2019). In this regard, TPs from psychiatric drugs have been effectively detected using different high-resolution mass spectrometry (HRMS) analyzers such as Orbitrap (Llorca et al., 2019) and quadrupole time-of-flight (QTOF) (Carpinteiro et al., 2017; Gonzalez-Gil et al., 2019; Osawa et al., 2019). Mass analyzers can be coupled to gas chromatography; however, a wider range of compounds with different chemical properties and polarities can be properly analyzed through liquid chromatography (Aceña et al., 2015). Thus, as demonstrated in Table 5, liquid chromatography coupled to mass spectrometry is the preferred technique for pharmaceutical degradation experiments because of its high sensitivity and selectivity. Other techniques such as nuclear magnetic resonance (NMR) together with HRMS have been also performed on isolated TPs to conclusively identify the TPs' structures (Kråkström et al., 2020).

The feasibility of water treatment methods needs to consider the TPs in terms of abundance, stability, and ecotoxicity; which is highly dependent on the degradation pathway. For example, in the human body the metabolization of carbamazepine (CBZ) results in the formation of dihydroxy-carbamazepine and carbamazepine epoxide as the main metabolites (Kråkström et al., 2020). On the other hand, as it is shown in Figs. 4a and 15 different TPs derive from the ozonation of CBZ, such as 1-(2-benzaldehyde)-4-hydro-(1H,3H)-quinazoline-2-one (BQM) and 1-(2-benzaldehyde) -(1H,3H)-quinazoline-2,4-dione (BQD), which are the main representative products. Contrastingly, laccase-mediated degradation processes have demonstrated the formation of a lesser number of TPs (in the range of 2–5). The main TPs derived from laccase-mediated biodegradation of CBZ are 10,11-dihydro-10,11-epoxy-CBZ (CBZE), 10,11-dihydro-10,11-dihydroxy-CBZ (CBZD), and acridone (Alharbi et al., 2019; Ji et al., 2016; Naghdi et al., 2018; Tufail et al., 2021). Similar results were obtained by Pylypchuk et al. (2020) using peroxidase enzymes (horseradish peroxidase and lignin peroxidase).

The differences in the TPs and their abundance have a significant effect on the toxicity of the resulting solution. In this regard, Donner et al. (2013) evaluated the toxicity of TPs formed during ultraviolet

Table 4
Biocatalysis of psychiatric drugs by isolated-immobilized enzyme biocatalysts.

Enzyme	Source	Support	Immobilization method	Immobilization yield (%)	Psychiatric drug	Type of sample solution	Remove conditions	Time (h)	Stability/ reusability	Removal/ Degradation (%)	Reference
Laccases	*Trametes versicolor*	Polyimide aerogels	Covalent	17.2	Carbamazepine[a,b]	Ultrapure water and secondary effluent	20 ng/mL of CBZ, 200 rpm, 25 °C,	24	7 cycles, 22%	74–76	Simón-Herrero et al., 2019
Laccases	*Trametes hirsuta*	PVDF/MWCNTs	Adsorption	38.31	Carbamazepine[a,b]	Ultrapure water	5 ppm of CBZ, 223 U/mL of catalysts, pH 5, 25 °C	4	5 cycles, 20%	95	Masjoudi et al., (2021)
Laccases	*P. ostreatus*	TiO_2	Covalent	63.7	Carbamazepine[a,b]	Ultrapure water	10 μM of CBZ, 0.1 U/mL of enzyme, pH 5.5, 25 °C	48	Not reported	~10	Ji et al., (2017)
Laccases	*Trametes versicolor*	Nanobiochar	Adsorption	41	Carbamazepine[a,b]	Ultrapure water and secondary effluent	20 ng/mL of CBZ, 20 mg of catalyst, 200 rpm, 25 °C	24	3 cycles, 70%	83–86	Naghdi et al., (2017)
Laccases	*Trametes versicolor*	Polyacrylonitrile−biochar	Covalent	Not reported	Carbamazepine[a,b]	Ultrapure water	2 ppb of CBZ, 25 °C, pH 4- 7	8	10 cycles, 17%	48.6	Taheran et al., (2017)
Laccases	*Trametes versicolor*	SiO_2	Covalent	35	Carbamazepine[a,b]	Ultrapure water	10 mb/mL of CBZ, 520 μM 25 °C, pH 7	4	7 cycles, ~28%	~50	Guardado et al., (2021)
Horseradish peroxidase and lignin peroxidase	Commercial enzymes	Fe_3O_4/SiO_2	Encapsulation	Not reported	Carbamazepine[a,b]	Ultrapure water	17.6 μg/mL of CBZ, 0.06 mg/mL of enzyme, pH 3–5,	72	20 cycles, 43–50%	60–100	Pylypchuk et al., (2020)
Soybean Peroxidase	Commercial enzymes	ZnO, TiO_2	Covalent	Not reported	Venlafaxine[a]	Mixture of pollutants	2 ppm of sample, 0.3 mM of H2O2, pH 4, 2 mg of biocatalyst, 25 °C	0.5	4 cycles, 95%	7.3–11.0	Morsi et al., (2021)

[1]Antidepressant.
[3]Antipsychotic.
[a] Anxiolytic.
[b] Mood stabilizer, Carbamazepine (CBZ), Polyvinylidene Fluoride (PVDF), Multiwalled carbon nanotubes (MWCNTs).

Table 5
Detection and monitoring techniques for transformation products of psychiatric drugs.

Psychiatric Drug	Degradation method	Technique	Transformation products	Representative transformation products	Reference
Carbamazepine[2,3]	Electro-Fenton	LC-QTOF-MS/MS	7	CBZE	(Li et al., 2021)
Carbamazepine[2,3]	Ozonation	LC-QTOF-MS and NMR	15	BQM BQD	Kråkström et al. (2020)
Carbamazepine[2,3]	UV/H_2O_2	HPLC-MS/MS	6	CBZE	Lu and Hu (2019)
Carbamazepine[2,3]	Biocatalytic (*Aspergillus oryzae* laccase)	LC-ESI-MS	5	NR	Tufail et al. (2021)
Carbamazepine[2,3]	Biocatalytic (*Trametes versicolor* laccase)	LDTD-MS	2	CBZE CBZD	Naghdi et al. (2018)
Carbamazepine[2,3]	Biocatalytic (*Trametes versicolor* laccase)	LC-LTQ-Orbitrap	3	CBZE CBZD Acridone	Ji et al. (2016)
Carbamazepine[2,3]	Biocatalytic (*Trametes versicolor* laccase)	LC-ESI-MS	2	CBZE Acridone	Alharbi et al. (2019)
Carbamazepine[2,3]	Biocatalytic (Horseradish peroxidase and lignin peroxidase)	NMR	2	CBZE CBZD	Pylypchuk et al. (2020)
Venlafaxine[1]	Photodegradation	LC-LIT-Orbitrap	~70	ODMVFX NDMVFX	Lambropoulou et al. (2017)
Venlafaxine[1]	Biodegradation (enzymes extracted from anaerobic sludge)	LC-QTOF-MS	0	NR	Gonzalez-Gil et al. (2019)
Venlafaxine[1]	Biodegradation (*Trametes versicolor*, *Ganoderma lucidum*, and *Pleurotus ostreatus*)	LC-LTQ Orbitrap	3	ODMVFX NDMVFX	Llorca et al. (2019)
Venlafaxine[1]	Photodegradation	UHPLC-QTOF-MS/MS	5	NR	Osawa et al. (2019)
Amitriptyline[1,2,3]	Photodegradation	UHPLC-QTOF-MS/MS	8	NR	
Trazadone[1]	Photodegradation	UHPLC-QTOF-MS/MS	7	NR	
Diazepam[2]	Chlorination	LC-QTOF-MS/MS	5	CMAB	Carpinteiro et al. (2017)
Oxazepam[2]	Chlorination	LC-QTOF-MS/MS	1	OXA-TP	
Nordazepam[2]	Chlorination	LC-QTOF-MS/MS	4	Phenylquinazoline products	
Alprazolam[2]	Photo-Fenton	LC-(ESI)MS/MS	15	4-Hydroxyalprazolam	Mitsika et al. (2021)
Diazepam[2]	Photo-Fenton	LC-(ESI)MS/MS	23	Nordiazepam Oxazepam Temazepam	

[1] (Antidepressant); [2] (Anxyolitic); [3] (Mood stabilizer); LC-QTOF-MS/MS (Liquid chromatography coupled to quadrupole Time-of-Flight Mass Spectrometry); NMR (Nuclear magnetic resonance); HPLC-MS/MS (High Performance Liquid Chromatography coupled with a Triple Quadrupole Mass Spectrometer; LC-ESI-MS (Liquid Chromatography-Electrospray Ionization-Mass Spectrometer); LDTD-MS (Laser Diode Thermal Desorption–Tandem Mass Spectrometry); LC-LTQ Orbitrap (Liquid Chromatography System coupled to a Hybrid Linear Ion Trap – High Resolution Mass Spectrometer); LC-LIT-Orbitrap (Liquid Chromatography coupled to a Linear Ion Trap Orbitrap Mass Spectrometer); LC-QTOF-MS (Liquid Chromatography Quadrupole Time-of-Flight Mass Spectrometry); UHPLC-QTOF-MS/MS (Ultra-High Performance Liquid Chromatography coupled to Quadrupole time-of-flight Mass Spectrometry); LC-(ESI)MS/MS (Liquid Chromatography-Electrospray Ionization-Mass Spectrometry); CBZE (10,11-dihydro-10,11-epoxy-CBZ); BQM (1-(2-benzaldehyde)-4-hydro-(1H,3H)-quinazoline-2-one); BQD (1-(2-benzaldehyde)-(1H,3H)-quinazoline-2,4-dione); NR (Not reported); CBZD (10,11-dihydro-10,11-dihydroxy-CBZ); ODMVFX (O-desmethylvenlafaxine); NDMVFX (N-desmethylvenlafaxine); CMAB (5-Chloro-2-(methylamino)benzophenone); OXA-TP (6-chloro-3,4-dihydro-4-phenyl-2-quinazolinone).

photolysis of CBZ. The ecotoxicity assays showed an increased ecotoxicity after CBZ degradation, demonstrating higher toxicity of the resulting TPs (Donner et al., 2013). Furthermore, the individual and mixture toxicity of four TPs of CBZ (CBZE, CBZD, BQD, and BQM) were tested in zebrafish (Danio rerio). The mixture presented comparable toxicity to that of CBZ, while the individual toxicity assessment suggested that BQM and BQD were the main ones responsible for the toxicity (Pohl et al., 2020). These results agreed with Alharbi et al. (2019), who compared the enzymatic method with advanced oxidation processes (ozonation, UV photolysis, and UV/H_2O_2 treatment) in terms of toxicity of treated solutions. Ozonation and UV photolysis of CBZ resulted in increased toxicity due to the formation of highly toxic TPs. However, the enzymatic degradation method produced a non-toxic effluent under the same toxicity assessment assay (Alharbi et al., 2016, 2019). Similarly, Tufail et al. (2021) evaluated the effect of adding an enzymatic pretreatment on the degradation of CBZ by ultraviolet photolysis. Interestingly, the non-enzymatic treatment produced twelve TPs, while the enzymatic treatment formed five TPs with lower abundance, suggesting a more complete degradation (Tufail et al., 2021). In this context, the merits of biocatalytic degradation are not only related to their low energy requirements and moderate conditions but also to the minimization of undesirable TPs due to the high specificity of enzymes (Naghdi et al., 2018).

On the other hand, the photocatalytic degradation of Venlafaxine (VFX) and the consequent formation of TPs have been investigated by different authors. Lambropoulou et al. (2017) detected more than 70 TPs from the photocatalytic degradation of VFX using 800 mg/L of TiO_2 catalyst. Whereas Osawa et al. (2019) elucidated the structures of five TPs derived from the photocatalytic degradation of VFX using 150 mg/L of modified cobalt-titanate nanowires as catalyst (Osawa et al., 2019). The remarkable differences in TPs formation could be attributed to the catalysts used, their concentration, among other operational parameters.

Typically, O-desmethylvenlafaxine (ODMVFX) and *N*-desmethylvenlafaxine (NDMVFX) are found as the main TPs of VFX' degradation (Lambropoulou et al., 2017; Llorca et al., 2019). ODMVFX is formed by the demethylation of the methoxy group of VFX, while the demethylation of the dimethylamino group of VFX results in the formation of NDMVFX. Recently, Llorca et al. (2019) evaluated the removal efficiency of three fungal treatments (*Trametes versicolor, G. lucidum*, and *Pleurotus ostreatus*) on VFX. Regardless of the fungal species, three TPs including ODMVFX and NDMVFX were reported. Similar VFX removal efficiencies (~70%) were achieved by *T. versicolor and G. lucidum*; however, the latter one produced more ODMVFX. Despite both TPs

(ODMVFX and NDMVFX) do not possess higher toxicity effects than those presented by the parent compound (VFX), ODMVFX had a higher N-nitro-sodimethylamine formation potential with negative effects on human health and the environment. Therefore, *T. versicolor* was presented as a better alternative in comparison with *G. lucidum*, which generated more ODMVFX within their TPs (Llorca et al., 2019).

In this manner, a critical issue for promoting the large-scale application of degradation methods requires not only to ensure an efficient degradation of the parent compounds but also to ensure their TPs are nontoxic. Finally, the detection of TPs derived from the degradation of other psychiatric drugs such Diazepam, Oxazepam, Nordazepam, Amitriptyline, Alprazolam, and Trazadone, are also found in the literature (Table 4) (Carpinteiro et al., 2017; Mitsika et al., 2021; Osawa et al., 2019).

6. Regulatory policies on prescription and environmental detection of psychiatric drugs

The determination of the presence of commonly prescribed drugs in aquatic environments began to be reported in the 1960s, and the first evidence of the effects on the environment and living organisms took more than 30 years to show that some drugs such as prescription drugs hormone replacement therapy and the contraceptive pill present in wastewater had effects such as feminization of fish (Daughton, 2016; Tyler et al., 1998).

With the growing array of medications and its increasing availability on the market, drug advertising and its regulations is important to individuals, societies, and environment (Geyer and Wang, 2019). Different factors are related in the way to create proper regulations in medicines, including people or institutions that control or direct, a principle, and a law or a method For example, since 1983, the US Food and Drug Administration (FDA) have substantially changed legislation and regulatory initiatives related to drugs approval (Darrow et al., 2020). In 2011, the FDA implemented Risk Evaluation and Mitigation Strategies (REMS), strategies that includes some requirements for the approval of drugs, including medication guide, health care information, and elements to ensure safe use and disposal (Darrow et al., 2020).

As usually happens, developed countries seems to have better regulatory policies related to global markets and its waste management. For example, in relation to pharmaceutical industry, the United Kingdom has had environment for prescription drug advertising and disposal for over 30 years. It is known that since 1974, the Association of British Pharmaceutical Industry (ABPI) began to provide guidelines that resulted in the current form that drug prescription and further disposal are handle. Guidelines that are in accordance with the Ethical Criteria for Medical Drug Promotion developed by the World Health Organization (WHO) (Geyer and Wang, 2019). In contrast, in developing countries, pharmaceutical laws and regulations are hardly applied. For example, even though the Food and Drug Organization (FDO) of Iran establishes regulatory policies for pharmaceuticals, dysfunction in the pharmaceutical systems, such as insufficient industry development, unaffordability of medicines, unregulated market of medicinal herbs, and illegal commercialization make harder to applied regulatory polices (Zaboli et al., 2016).

As it is known, hospitals are one the principal sources of releasement of pharmaceuticals into the environment, which depends primarily in some factors as number of patients, beds, facility size and urbanization level (Carraro et al., 2016). Thus, regulations in terms of waste management in hospitals becomes of crucial importance. The hospitals wastes are classified by the WHO in different streams, in which pharmaceutical waste is included (Ali et al., 2017). Along the world, different directives, and guidelines for the management of pharmaceutical residues of hospital effluents are reported. For example, in Europe, the European Decision n. 532 of May 2000 (EU, 2000/532/CEE) stated that pharmaceuticals residues must not be discharged into a foul sewer but treated as waste and collected and disposed as such. Moreover, some other regulatory policies in different countries are specified for the waste management of pharmaceuticals, such as the resolution n. 430 of 13 May 2011 of Brazil (Ministerio do Meio Ambiente Conselho Nacional do Meio Ambiente, 2011), the GB8978-88 law in China (National Standard of the People's Republic of China, 1998), and the Bio-medical Waste (Management & Handling) Rules of 20 July 1998 in India (Ministry of Environment and Forests, 1998).

Environmental contamination by psychiatric substances is a problem of emerging concern that has not received due attention in terms of the negative effects they can generate. Currently there is no legislation or regulations for the control, detection or degradation of psychiatric substances, since it is a problem that has to be approached interdisciplinary to integrate different knowledge and be effective (Argaluza et al., 2021).

Even so, the European Union Water Framework Directive includes a very limited number of compounds on its "Watch List" of priority substances monitored under environmental regulations (Aydın et al., 2021). Recently, the antidepressants venlafaxine and desvenlafaxine were considered for inclusion in the "Watch List" under the European Union Water Framework Directive, being the first psychiatric drugs to be included in this list (Cortes et al., 2020; "European Commission," 2020; Lertxundi et al., 2021).

Different strategies can be implemented to reduce the presence of psychiatric substances in the environment: promoting prescription and responsible consumption, developing pharmaceutical products that are more ecological or biodegradable, improving pharmaceutical waste management and developing new treatment processes of wastewater to improve the efficiency of the WWTP in the degradation of pharmaceutical substances. The education of the population and health professionals, together with the collaboration of experts in environmental sciences, are extremely essential for progress to generate regulations that allow reducing the presence of pharmaceutical substances in the environment (Argaluza et al., 2021).

7. Conclusions and future remarks

Psychiatric drugs removal from aquatic systems has gained attention due to the increasing demand of these medications during the COVID-19 pandemic, which according to literature has affected the human mental health by the increment in cases of depression, stress, and anxiety. The presence in aquatic systems during the pandemic has been achieved, it has been demonstrated that WWTPs are unable to degrade these drugs since their effluents presents almost the same concentration than their influents. Moreover, the effects over humans, flora and fauna have revealed that even small concentration (ng/L-mg/L) of psychiatric drugs might promotes negative physiology, and metabolic effects, and changes behavior.

Different techniques might be implemented to solve this environmental issue, including conventional or non-biocatalytic technologies, which can be both physical and chemical techniques. Even though physical and chemical technologies are effective for the removal of psychiatric drugs in water, additional chemicals and equipment are usually required, making implementation difficult in real-world settings. Moreover, some techniques produce undesired transformation products, which might possess higher toxicity levels.

Thereby, biocatalytic processes, such as whole-cell biocatalysis, enzymatic biocatalysis, and nanobiocatalysis seem to be a better option to remove psychiatric drugs from aquatic systems since it is considered a green and sustainable process. In addition to the lower energy requirements, the production of undesirable transformation products is typically minimized due to the high specificity of enzymes. Despite their multiple benefits, further investigations are needed to overcome their current drawbacks, which are mainly associated with scalability issues and lower biodegradation rates in comparison to other technologies. The effectiveness of biocatalytic processes might be improved by the design of novel biocatalysts; for this, different enzymes and immobilization

techniques should be studied to obtain biocatalysts with enhanced specificity and catalytic activity toward psychiatric drugs. Also, further research is needed to evaluate the effectiveness of the proposed biocatalytic techniques using a broad range of molecules under different conditions. Typically, contaminated water is composed of a mixture of pollutants; thus, the degradation activity should be tested considering the presence of co-existing substances. Moreover, the performance of biocatalytic systems should be measured in real and complex contaminated water systems. On the other hand, scale-up is an important challenge in biocatalytic processes; thus, research efforts should be focused on this aspect. For instance, separation and purification processes are critical stages to define the feasibility of implementation as a tertiary treatment in WWTPs.

In addition to remediation actions, a prevention approach must be also considered to avoid the release of drugs into the environment. In this aspect, regulations that promote proper consumption, rational drug use, and adequate disposal practices are highly required. Finally, it is important to point out that the implementation of regulations and biocatalytic-assisted technologies will not only be effective to deal with the environmental effects of the COVID-19 pandemic but also in mitigating future effects associated with emerging medicines for possible upcoming medical emergencies.

Credit author statement

Saúl Antonio Hernandez Martínez: Writing-Original Draft, Figures, Tables, Data Curation. **Elda M. Melchor-Martínez**: Conceptualization, Methodology, Reviewing and Editing, Supervision, Project administration. **Reyna Berenice González-González**: Writing-Original Draft, Tables. **Juan Eduardo Sosa-Hernández, Rafael G. Araújo, Jesús Alfredo Rodríguez-Hernández and Damià Barceló**: Writing-Original Draft, Reviewing and Editing. **Roberto Parra-Saldívar**: Conceptualization, Reviewing and Editing, Resources. **Hafiz M. N. Iqbal**: Conceptualization, Reviewing and Editing, Supervision, Project administration.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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