TREATMENT METHODS FOR 1,2,4-TRIAZOLE FUNGICIDES FROM WATERS

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Fungicides are chemical compounds that are used to efface or avert the growth of fungi or their spores. According to the origin of fungicides, Rachid Rouabhi (2010) categorized them in two main groups of fungicides; 1. Biologically based fungicides (biofungicides): Include living microorganisms (bacteria, fungi) that are antagonistic to the pathogens that induce turf disease. Examples: Ecoguard contains *Bacillus licheniformis*; Bio-Trek 22G contains *Trichoderma harzianum*. In the case of a biofungicide, the Latin name of the microbe that it contains is the generic name of the fungicide. 2. Chemically based fungicides: Synthesized from organic and inorganic chemicals, most of the fungicides that are sold throughout the world are chemically-based (Rouabhi, 2010). In addition; fungicides, protective fungicides (Copper Fungicides, Dithiocarbamates, Phthalimides, Halogenated Compounds, Sulphurous fungicides) and systemic fungicides (1. Alkylalanines, 2. Benzimidazoles, 3. Hydroxypyrimidines, 4. Carboxamides, 5. Conazole Group Fungicides (i. Imidazoles, ii. Triazines), 6. Other Derivatives) are classified into two major groups.

The pesticides and fungicides remaining on the soil surface enter the surface flow with rain water or by leaching from the ground water and other soil and then they reach water sources. Also, these chemicals can be collected from wastewater generated as a result of domestic and industrial activities. These components, which mix with the receiving waters and affect people through the food chain, must be removed from the water after use. To protect the safety of human health and aquatic ecosystems, European Union Directive has regulated the limits for individual pesticide and for the sum of all pesticides, this includes insecticides (insects),

herbicides (weeds), and fungicides (fungi), in drinking water are 0.1 μg/L and 0.5 μg/L, respectively (Liu et al., 2017).

Azole compounds are some of the most widely used fungicides worldwide and are used as anti-icing fluids, wood preservatives, and adhesives (Huang, Zhao, et al., 2022). Modern systemic fungicides are typified by the triazoles. This chemical family of fungicides, introduced in the 1980s, consists of numerous members: difenoconazole, fenbuconazole, myclobutanil, propiconazole, tebuconazole, tetraconazole, triadimefon, and triticonazole (Rouabhi, 2010). A triazole is a heterocyclic compound featuring a five-membered ring of two carbon atoms and three nitrogen atoms with molecular formula $C_2H_3N_3$. These may be of two types, the 1,2,3-triazoles or r-triazoles (Figure 1) and the 1,2,4- triazoles or s-triazoles (Figure 2) (Potts, 1961). 1,2,3-Triazoles are one of the most important nitrogen-containing five-membered heterocycles and have a wide range of applications in pharmaceuticals, supramolecular chemistry, organic synthesis, chemical biology and industry (Ali, 2020). 1,2,4-Triazole exists in two tautomeric forms known as 1*H*-1,2,4-triazole and 4*H*-1,2,4-triazole and it is very difficult to separate them due to their rapid interconversion. The 1*H*-1,2,4-triazole compounds are considered interesting heterocycles since they possess important pharmacological activities such as antifungal and antiviral activities (Al-Masoudi et al. 2006).
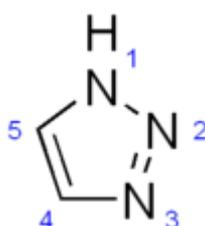
Figure 1. 1,2,3-triazole
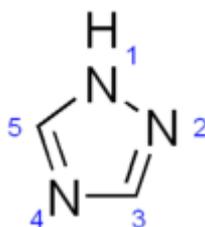
Figure 2. 1,2,4- triazole

15,519.06 Tons of triazoles and diazoles were used in 2014. For instance, in the United States, approximately 2.5 million pounds of propiconazole and 2.1 million pounds of tebuconazole

were used in agriculture purposes. The widespread application of triazoles causes them to enter aquatic environments through runoff, agricultural returns, groundwater intrusions, or through plant uptake. Therefore, triazole fungicides have been frequently detected in aquatic ecosystems all around the world. Huang et al. (2022) have tabulated the measured concentrations of triazole fungicides in waters (Huang, Jiang, et al., 2022). According to the given Table 1, levels are generally in the 100–500 ng/L range for many triazoles and many bodies of water while the levels can increase upwards of 1000 ng/L at around golf courses and in sewage effluent. These levels can cause substantial risks to environmental ecosystems and aquatic life.

Table 1. The measured concentrations of triazole fungicides in waters (extracted from the study of Huang, Jiang, et al., 2022)

Triazoles	Sampled sites	Concentration
Difenoconazole	Surface water in River Madre de Dios, Costa Rica	0.36 µg/L
Difenoconazole	Agricultural water in Thailand (Salakru, NongSua)	28 µg/L
Difenoconazole	Surface water in Malaysia (Kedah)	300 µg/L
Difenoconazole	Surface water in Victoria, Australia	0.15 µg/L
Difenoconazole	Surface water in River Meolo, Italy	0.0095 µg/L
Difenoconazole	Surface water in Jiulong River Estuary, China	0.125 µg/L
Fenbuconazole	Waterworks of Xiamen city, China	0.00022–0.00698 µg/L
Myclobutanil	River Madre de Dios, Costa Rica	0.17 µg/L
Myclobutanil	Surface waters in the Yarra catchment, VIC, Australia	>0.2 µg/L
Paclobutrazol	Surface water in Jiulong River Estuary and West Xiamen Sea, China	0.1196 µg/L
Paclobutrazol	Groundwater on golf courses throughout the United States and Canada	4.2 µg/L
Propiconazole	Banana plantation, Limon, Costa Rica	0.15–13 µg/L
Propiconazole	Influent of pharmaceutical company, Belgium	0.17–0.24 µg/L
Propiconazole	Effluent of pharmaceutical company, Belgium	0.012–0.14 µg/L
Propiconazole	Paris sewer, France	0.15–0.21 µg/L
Propiconazole	Raw municipal wastewater, Western Balkan Region	< 0.08 µg/L
Propiconazole	River Madre de Dios, Costa Rica	0.13 µg/L
Propiconazole	Effluent of wastewater treatment plants in Belgium	0.0019–0.1783 µg/L
Propiconazole	Agricultural surface water in 13 states of US	0.291–1.150 µg/L
Propiconazole	Wastewater treatment plants influents, Switzerland	0.001–0.03 µg/L
Tebuconazole	Wastewater treatment plants influents, Switzerland	0.001–0.03 µg/L
Tebuconazole	River Madre de Dios, Costa Rica	0.27 µg/L
Tebuconazole	Morcille catchment, France	0.011–6.5 µg/L
Tebuconazole	Runoff events in the west of France	81 µg/L
Tebuconazole	Stream water in Morcille River, France	175–200 µg/L
Triadimefon	Rivers in China	0.00152 to 5.22 µg/L
Triadimefon	Surface runoff in the USA	922 µg/L
Triadimenol	River Madre de Dios, Costa Rica	0.1 µg/L

The interaction degrees with the environment of the fungicides depend on their physicochemical properties. Their mobility and persistence in the soil, dissociation in water, bioaccumulation, and durability in the environment are significantly effected from the physicochemical properties. So, the physicochemical properties of triazole fungicides are very important for their environmental fate. Table 2 shows the physicochemical properties of 1,2,4-triazole fungicides such as IUPAC names, MW—molecular weight, logP—partition

coefficient, HBD—hydrogen bonds donors, HBA—hydrogen bonds acceptors, RBC—rotatable bonds count, TPSA-topological polar surface area, DT50and DT90the periods after that 50% and respectively 90% of the fungicide to be degraded. It can be concluded from Table 2 that the given 1,2,4-triazole fungicides are partly lipophilic (the median lop P is 3.35), partly flexible (the median value of the rotatable bonds is 5) and their hydrogen bonding capacity is quite low. Their lower mobility and higher sorption into soil due to their hydrophobic nature and low molecular weight may cause to the persistence of them in soil (Roman et al., 2021).

Table 2. The physicochemical properties of the fungicides (extracted from the study of Roman et al. (2021))

Fungicide Common Name	IUPAC Name	MW (g/mol)	logP	HBD	HBA	RBC	TPSA ($Å^2$)	DT$_{50}$ for Field Studies (Days)	DT$_{90}$ for Field Studies (Days)
Cyproconazole	2-(4-chlorophenyl)-3-cyclopropyl-1-(1,2,4-triazol-1-yl)butan-2-ol	291.77	2.9	1	3	5	50.9	62.1–501.2 (persistent)	179–1000
Difenoconazole	1-[[2-[2-chloro-4-(4-chlorophenoxy)phenyl]-4-methyl-1,3-dioxolan-2-yl]methyl]-1,2,4-triazole	406.3	4.0	0	5	5	58.4	20–265 (persistent)	68–879
Epoxiconazole	1-[[3-(2-chlorophenyl)-2-(4-fluorophenyl)oxiran-2-yl]methyl]-1,2,4-triazole	329.8	3.2	0	4	4	43.2	0.75–247.8 (persistent)	183.7–10.000
Flutriafol	1-(2-fluorophenyl)-1-(4-fluorophenyl)-2-(1,2,4-triazol-1-yl)ethanol	301.29	2.3	1	5	4	50.9	316–4089 (very persistent)	1051–13,583
Hexaconazole	2-(2,4-dichlorophenyl)-1-(1,2,4-triazol-1-yl)hexan-2-ol	314.2	3.7	1	3	6	50.9	49–200 (persistent)	NA
Metconazole	5-[(4-chlorophenyl)methyl]-2,2-dimethyl-1-(1,2,4-triazol-1-ylmethyl)cyclopentan-1-ol	319.8	3.7	1	3	4	50.9	26.6–368.5 (persistent)	102.9–1000
Myclobutanil	2-(4-chlorophenyl)-2-(1,2,4-triazol-1-ylmethyl)hexanenitrile	288.77	2.9	0	3	6	54.5	9–58 (Moderately persistent)	637–1906
Paclobutrazol	1-(4-chlorophenyl)-4,4-dimethyl-2-(1,2,4-triazol-1-yl)pentan-3-ol	293.79	3.2	1	3	5	50.9	27.2–60.8 (persistent)	46.7–202
Propiconazole	1-[[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl]methyl]-1,2,4-triazole	342.2	3.5	0	4	5	49.2	15.3–96.3 (moderately persistent)	108–525
Tebuconazole	1-(4-chlorophenyl)-4,4-dimethyl-3-(1,2,4-triazol-1-ylmethyl)pentan-3-ol	307.82	3.7	1	3	6	50.9	25.8–91.6 (moderately persistent)	66–304
Tetraconazole	1-[2-(2,4-dichlorophenyl)-3-(1,1,2,2-tetrafluoroethoxy)propyl]-1,2,4-triazole	372.14	4.4	0	7	7	39.9	136–1688 (moderately persistent)	453–5606
Triadimenol	1-(4-chlorophenoxy)-3,3-dimethyl-1-(1,2,4-triazol-1-yl)butan-2-ol	295.76	3.1	1	4	5	60.2	24.1–83.7 (persistent)	76.3–423.9
Triadimefon	1-(4-chlorophenoxy)-3,3-dimethyl-1-(1,2,4-triazol-1-yl)butan-2-one	293.75	2.8	0	4	5	57	26 (non-persistent)	NA
Triticonazole	(5E)-5-[(4-chlorophenyl)methylidene]-2,2-dimethyl-1-(1,2,4-triazol-1-ylmethyl)cyclopentan-1-ol	317.8	3.1	1	3	3	50.9	36.1–242 (persistent)	329–803

Triazoles having antifungal effects inhibit the ergosterol biosynthesis, thereby interfering with the formation of fungal cell-wall. They contain about 25 commercial agrochemicals worldwide and are widely used due to their excellent antifungal activity and relatively low resistance risk. However, potential endocrine-related side effects on humans and wildlife occur owing to their large consumption because they prevent the cytochrome P450-dependent 14 α-demethylase, an enzyme counted in the biosynthesis of steroid hormones, and then disturb the balance of

androgens and estrogens. Triazoles exhibit high chemical and photochemical stability and low biodegradability, making them permanent and accumulated in the environment; so, it has been considered that they are hazardous to the environment and human health (Huang, Jiang, et al., 2022). For these reasons, the treatment process of the waters including triazoles should be developed in order to minimize the adverse effect of them. In the literature, the treatment processes such as adsorption, degradation, biodegradation, photocatalytic degradation, electrochemical oxidation, membrane filtration, and nanofiltration have been evaluated for the removal of 1,2,4-triazole fungicides. The studies in the literature about the treatment methods used for the removal of 1,2,4,-triazole fungicides from waters were summarized as follows.

The treatment methods used for the removal of 1,2,4-triazole fungicides

Adsorption

Fang et al. (2019) investigated the adsorption of three commonly used triazole fungicides namely hexaconazole (HEX), myclobutanil (MYC), and triadimenol (TRI) on pristine polystyrene (PS) particles as adsorbent. They have chosen PS as the model adsorbent material representing microplastics because it is an abundant type in wastewater treatment plants arising from pharmaceuticals and personal care products. The reason for choosing these triazole fungicides is high sales of them and also having the basic chemical structure of triazole fungicides and some characteristic groups. The linear forms of Pseudo-first order, Pseudo-second-order, and Intraparticle diffusion models were applied to the adsorption data and the results showed that Pseudo-second-order model was found to be more proper for describing the adsorption kinetics process of the three triazole fungicides on PS. Intraparticle diffusion model confirmed that adsorption and subsequent pore filling may drive the adsorption. The adsorption isotherm models of Langmuir and Freundlich were used to predict the distribution of the triazole fungicides at adsorption equilibrium between solid and liquid phases. Accordingly, it was observed that Freundlich model was more fitted to the equilibrium data indicating the heterogeneity in the adsorption process. The effects of chemical structure, particle size, pH value, and ionic strength on adsorption capacity was investigated and the results showed that the adsorption capacity of PS increased with the decrease in PS particle size and change in solution pH value and increase in salt ion strength. The discussion of the main adsorption mechanisms was further done by analyzing ATR-FTIR peaks of PS before and after adsorption and also influencing factors. Accordingly, the main mechanisms of adsorption were observed to be hydrophobic and electrostatic interactions. Furthermore, the order of adsorption and

desorption capacity of PS was HEX > MYC > TRI and also it was found that the adsorption capacity of PS for three triazole fungicides reached ug/g level. All results of this work indicated that PS can effectively adsorb these triazole fungicides with the high capacity (Fang et al., 2019).

In the study of Wang et al. (2019), the graphene was decorated by Fe_3O_4 nanoparticles and utilized as an adsorbent for the removal of ten commonly used triazole fungicides in agriculture, namely tebuconazole, hexaconazole, flutriafol, triadimenol, triazolone, epoxiconazole, penconazole, myclobutanil, paclobutrazol, and metconazole from aqueous solutions. The graphene/Fe_3O_4 NPs composite was chosen as an adsorbent due its magnetic property providing easy separation from the aqueous solution and improved adsorption capacity. The adsorption percentages of ten fungicides (20 μg/mL) ranged from 85.2% to 96.0% at the adsorbent concentration of 0.4 g/L. The effect of environmental conditions such as contact time, adsorbent amount, solution pH, and ionic strength were investigated and the results showed that the adsorption capacity of graphene/Fe_3O_4 NPs composite was not affected by the solution pH and ionic strength. The study on adsorption kinetics and thermodynamics were investigated by taking tebuconazole as an example because of the highest adsorption capacity. The pseudo-first-order and pseudo-second- order models were applied to the experimental data at different temperatures. The linear analysis results indicated that the pseudo-second-order model was more suitable to describe the adsorption of tebuconazole on graphene/Fe_3O_4 NPs composite due to the higher regression coefficients and the closeness between the calculated adsorption amount at the equilibrium ($q_{e,cal}$) and the experimental values ($q_{e,exp}$). Weber-Morris model plots exhibited multi-linearity suggesting that the whole adsorption process was limited by both external mass transfer and intra-particle diffusion. Langmuir and Freundlich isotherm models were applied to the equilibrium data of the adsorption of tebuconazole on graphene/Fe_3O_4 NPs composite and it was found that Langmuir isotherm model fitted better than Freundlich isotherm model indicating the monolayer and homogeneous adsorption process. In addition, the maximum adsorption capacity of tebuconazole onto graphene/Fe_3O_4 NPs composite was calculated as 60.2, 70.3, 80.5 mg/g at 273, 293 and 313 K, respectively. In the thermodynamic study, free energy of adsorption, enthalpy, and entropy were calculated and the results showed that the adsorption is a spontaneous, endothermic, and physisorption process. With the content of investigating the possible interactions in the adsorption, the electrostatic interaction, hydrogen bonding interaction, π- π stacking, hydrophobic interaction, and cation- π interaction

were discussed and it was concluded that π-π stacking was observed to be the dominant factor for the adsorption of tebuconazole on graphene/Fe_3O_4 NPs composite (Wang et al., 2019).

Crini et al. (2017) used two conventional activated carbons (ACs) and five non-conventional cross-linked cyclodextrin (CD)-based materials (α-CDP, β-CDP, γ-CDP, $\alpha\beta\gamma$-CDP mixture, and hydroxypropyl-β-CDP) as adsorbents for the removal of triazole fungicides from aqueous mixtures of propiconazole (PROPI), tebuconazole (TEBU), epoxiconazole (EPOXI), bromuconazole (BROMU) and difenoconazole (DIFENO) which have used in wide areas such as wood industry, vegetable cultivation, horticulture, and agriculture in order to protect various products against fungal decay. The adsorption experiments were conducted at 1.0 mg/L fungicide concentration, 5.0 initial pH, 1.0 g/L adsorbent concentration, 4.0 h contact time, and 25 $^{\circ}$C temperature using batch method. The obtained adsorption percentages for 9 adsorbents were presented in Figure 3. It was observed that the modified forms of activated carbon (M-PAC and M-GAC) were more efficient than their raw forms (PAC and GAC) and the CD-based materials regardless of triazole type. The adsorption of fungicides on AC occurs via dispersive interactions between the π electrons in the aromatic ring of the fungicides and the π electrons in the carbons, by physical adsorption in the carbon network, and by hydrogen bonding. The differences between the adsorption percentages of the commercial AC and modified AC resulted from the surface charge character. Accordingly, the AC modified with NaOH had less acidic characters than the commercial ACs, which favored adsorption process. For the adsorption of fungicides on CD-based materials, the adsorption mechanism is more complicated. The steps of surface adsorption, diffusion into polymer network, and chemisorption are considered to be effective simultaneously (Crini et al., 2017).
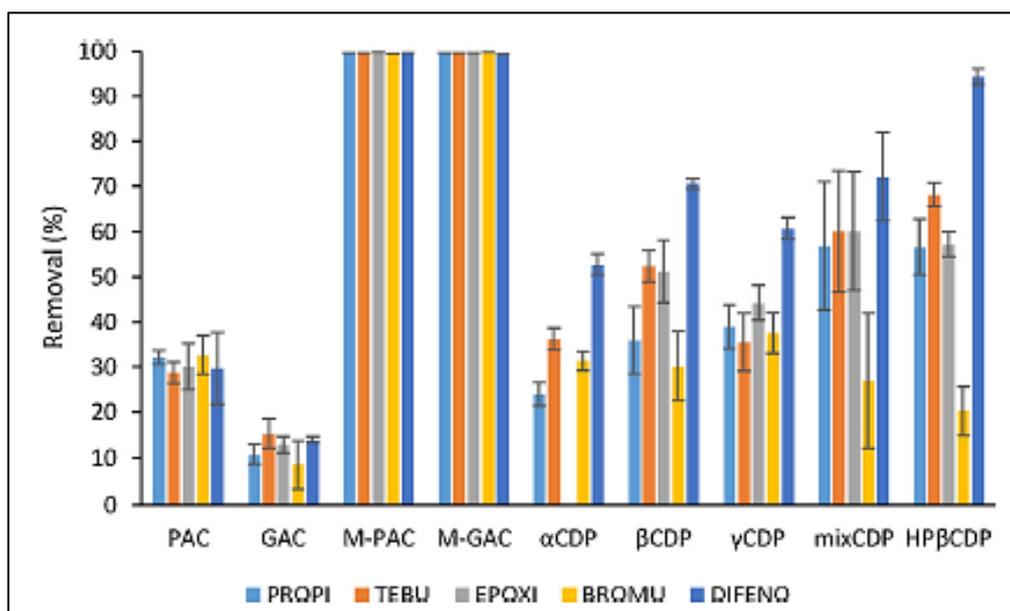
Figure 3. The adsorption percentages of PROPI, TEBU, EPOXI, BROMU, DIFENO on commercial activated carbons (Panreac powdered form (PAC) and Chemviron CA201 granular form (GAC)), activated carbons modified with NaOH (M-PAC, M-GAC), and cross-linked cyclodextrin (CD)-based materials (α-CDP, β-CDP, γ-CDP, αβγ-CDP mixture, and hydroxypropyl-β-CDP)

It was observed that the removal percentages increased as the adsorbent concentration increased due to the availability of more adsorption sites regardless of the adsorbent. Also, the removal percentages increased with contact time for all triazole fungicides, reaching an equilibrium within 3h for M-GAC and only 20 min for HPβCDP.

Table 3 showed the removal percentages of triazole fungicides in a mixture or in single solution for M-GAC and HPβCDP. It was clearly seen that there was no competition effect with the use of M-GAC while strong competition prevailed among fungicides for binding sites with the use of HPβCDP (Crini et al., 2017).

Table 3. The removal percentages of triazole fungicides in a mixture (concentration of each triazole=1.0 mg/L, 5.0 mg/L in total) or in single solution (concentration=5.0 mg/L) for M-GAC and HPβCDP (other conditions: adsorbent concentration=1.0 g/L, contact time=4h; T=25°C)

	PROPI	TEBU	EPOXI	BROMU	DIFENO
M-GAC					
in mixture	99.7 ± 0.3	99.7 ± 0.3	99.7 ± 0.2	99.8 ± 0.5	99.4 ± 0.3
alone	99.6 ± 0.9	94.8 ± 0.9	90.6 ± 0.7	82.8 ± 0.9	99.8 ± 0.2
HPβCDP					
in mixture	56.6 ± 1.7	68.2± 2.6	57.2 ± 1.5	20.3 ± 1.3	94.3± 1.9
alone	50.0 ± 2.1	81.0± 0.6	25.4 ± 2.3	60.7 ± 3.2	99.1± 1.4

The study of Amorim et al. (2013) was conducted in Brazil, where is the largest worldwide producer and exporter of coffee and they have studied on the pesticides used in coffee industry. One of the pesticides is epoxiconazole belongs to the class of triazoles, which is used for the control of coffee rust. 1,2,4-triazole is formed as a result of the degradation of epoxiconazole in the environment and it has environmental risk due to its being highly soluble and stable in water. It has been known that the conventional water treatment processes such as coagulation, chemical oxidation are not proper for the removal of various organic compounds such as pesticides. Therefore, in this study, adsorption was preferred for the removal of epoxiconazole due to its being relatively simple, effective, and economic feasible technique among the other removal processes used for pesticide removal like photocatalytic degradation, biogological oxidation, advanced oxidation process, aerobic-anaeorbic degradation, nano-filtartion membranes, and ozonation. Two commercial activated carbons namely charcoal-powdered activated carbon (CPAC) and bovine bone-powdered activated carbon (BPAC) were utilized as adsorbent for the removal of epoxiconazole. The results of adsorption kinetics showed that the pseudo-second-order model had higher regression coefficients and the calculated values ($q_{e,cal}$) from the pseudo-second-order model were closer to that obtained experimentally ($q_{e,exp}$). The equilibrium data of CPAC was well represented with Langmuir isotherm model while Freundlich isotherm model was found be the best fit for the equilibrium data of BPAC. Under the set experimental conditions, the removal percentages of CPAC and BPAC were found to be 76% and less than 8%, respectively. Therefore, it was observed that BPAC was not efficient

adsorbent for the removal of epoxiconazole. In the conclusion, the authors emphasized that although CPAC could be used for the removal of epoxiconazole, detailed studies should be done in order to obtain higher removal percentage and ensure the correct design of water treatment unit (Amorim et al., 2013).

Degradation

Ghauch (2008) investigated the degradation of flutriafol, a high persistent water/soil triazole pesticide, in water by zero-valent iron (ZVI) powder using a laboratory scale device consisting of a 20 ml pyrex serum vials fixed to a Vortex agitator at pH 6.6 and room temperature. Flutriafol is generally used in coffee, maize and cereals for the control of major seedborne and soil-borne diseases. Due to its high spray application rate and commonly usage on cereals, it is thought to cause water pollution. This study evaluated the usefulness of ZVI powder on the degradation of flutriafol in a phosphate buffered solution (PBS) at room temperature. The effect of iron concentration and dissolved oxygen, the observed degradation rates, the half-live of flutriafol, and the identification of some of the obtained by-products were investigated. The results showed that the half-live $t_{1/2}$ decreased from 10.8 ± 0.5 min to 3.8 ± 0.2 min as the concentration of ZVI raised from 10 to 50 g/L. According to the results of the effect of dissolved oxygen, the degradation of flutriafol occurred at a low concentration of dissolved oxygen as well as under a slightly acidic condition in the presence of an adequate buffer. Flutriafol degradation reactions progressed with first order kinetic with a half-live of about 10.8 ± 0.5 min and 3.6 ± 0.2 min at ZVI concentration of 10 g/L into oxygenated and anoxic solutions, respectively. UV–Vis spectrophotometer, a high performance liquid chromatography (HPLC) coupled with a photo diode array (PDA) and fluorescence detectors, a similar HPLC coupled with a PDA and a mass spectrometer detectors equipped with an atmospheric pressure photoionization source were used for monitoring the degradation of flutriafol and revealing by-products behaviors. Accordingly, a complete disappearance of flutriafol after 20 min of contact with ZVI, the loss of fluorescence properties of the final by-products, the defluorination of the triazole pesticide occurred via hydroxylation reaction and finally the hydrogenation of the triazole ring (Ghauch, 2008).

In the study of Saadaoui et al. (2021), the researchers investigated the degradation of two triazole pesticides (Myclobutanil and Penconazole) in aqueous solution by gamma irradiation. The effects of irradiation dose, pH, radical scavenger, and natural organic matter were examined on the removal of Myclobutanil and Penconazole. The removal percentage was acquired at least

90% at an absorbed dose of 0.575 kGy and 0.460 kGy for Myclobutanil and Penconazole, respectively. As increasing of dose, the removal percentage increases and the degradation takes place better under neutral conditions. When the concentration of humic acid was increased from 0 to 20 mg/L at a dose of 1.2 kGy, the removal percentages decreased from 100% to 40.67% and to 50% for Myclobutanil and Penconazole, respectively. When used thiourea as a radical scavenger, the degradation reaction of triazole pesticides was enhanced due to the active species like e_{aq}^- and ●H. HPLC-QTOF-MS/MS was used for the identification of the degradation by-products. Accordingly, five by-products were identified for Myclobutanil and ten for Penconazole and dominantly hydroxylation caused the formation of these by-products. A toxicity study was conducted on Wistar rats in order to evaluate the effects of these by-products, and it was found that no increase in toxicity was observed as a result of the degradation of two triazole pesticides. ^{1}HNMR analysis was conducted for the investigation of the mineralization of both pesticides by gamma irradiation and completely mineralization of both pesticides was achieved at 1.2 kGy. The overall results suggested that Gamma irradiation seems to be a promising method for the degradation of triazoles in water which can be used as recycled water (Saadaoui et al., 2021).

Zendegi-Shiraz et al. (2021) have focused on the removal of triazole fungicides namely penconazole, hexaconazole, and diniconazole via adsorbent-catalyst coupling (ACC) process. For this purpose, adsorption, degradation, and both of them were investigated separately with Ag and Fe_3O_4 as catalyst and PEG-CuO as adsorbent for the removal of the triazole fungicides. The results showed that a complete removal could not be achieved with the use of the catalyst alone, even at their high concentrations. On the other hand, the simultaneously use of PEG-CuO as adsorbent and one of the catalysts (Ag or Fe_3O_4) provided the completely removal of the triazole fungicides thanks to the ACC process. After obtained these findings, the effects of adsorbent load, catalyst load, ratio of catalyst to adsorbent, salt concentration, pH, and operating time were examined on the efficiency of ACC process for the removal of the triazole fungicides. Accordingly, the completely removal could be achieved for all triazole fungicides for 50/50 ratio of Ag/PEG-CuO as well as 30/70 ratio of Fe_3O_4/PEG-CuO. All triazole fungicides were completely removed at the absence of salt (NaCl). The optimum pH and operation time were obtained as 7.0 and 85 min, respectively. The experiments were conducted with the real fungicide polluted wastewaters obtained by washing some vegetables such as cucumber, lettuce, bell pepper, cabbage, and tomato at the optimum conditions of ACC process. The amounts of fungicide residues in vegetable wash wastewater before and after ACC process was

presented in Table 4. Accordingly, it can be concluded that the treatment of real fungicide polluted wastewaters could be effectively carried out at the obtained optimum conditions of ACC process. As a consequence, this study suggests the ACC process as a promising alternative for the removal of the triazole fungicides (Zendegi-Shiraz et al., 2021).

Table 4. The amounts of fungicide residues in vegetable wash wastewater before and after ACC process

Vegetable samples	Before treatment Penconazole Concentration (μg/mL)	Before treatment Hexaconazole Concentration (μg/mL)	Before treatment Diniconazole Concentration (μg/mL)	After treatment All fungicides Concentration (μg/mL)
Cucumber	3.25	2.59	1.49	n.q[a]
Tomato	n.q[a]	n.q[a]	n.q[a]	n.q[a]
Bell pepper	1.77	0.60	0.85	n.q[a]
Cabbage	3.50	n.q[a]	n.q[a]	n.q[a]
Lettuce	3.80	n.q[a]	n.q[a]	n.q[a]

[a]Not quantified: HPLC-UV did not detect fungicides.

Biodegradation

Liu et al. (2019) have aimed to isolate 1H-1,2,4-triazole (TZ) degrading strain from activated sludge acclimated by TZ. It was successfully done and identified as *Raoultella sp.* NJUST42. The efficiency of *Raoultella sp.* was investigated with regards to biodegradation of TZ, TOC removal, NH_4^+ release, pH increase, and biotoxicity reduction. The effects of initial TZ concentration, incubation temperature, initial pH and additional carbon source were also investigated on TZ biodegradation by *Raoultella sp.* Accordingly, the removal of TZ increased with increasing initial TZ concentration; however, it was found that TZ exhibited an inhibitory substrate at high TZ concentration. The optimum incubation temperature was observed as 30 ^{o}C, and too high or too low incubation temperature would adversely affect TZ biodegradation. It was also obtained that the optimum pH was 7.0 and both acidic and alkaline condition was unfavorable for TZ biodegradation. In the effect of additional carbon sources; a DT_{50} minimum value of 100.4 ± 8.4 h was obtained at the glucose concentration of 500 mg/L while that value reached a maximum value of 223.5 ± 18.4 h at the glucose concentration of 2000 mg/L, which indicated the competitive inhibition exerted by additional carbon source. As a consequence, the completely removal was achieved at incubation temperature of 30 °C, initial pH of 7.0, and initial concentration of 100 mg/L within 288 h. At these conditions, obvious TOC removal, NH_4^+ release, pH increase, biomass growth, biotoxicity reduction, and excitation emission matrix variation were also obtained. The first-order degradation kinetic model was in good

agreement with the TZ biodegradation profile by *Raoultella sp.*. HPLC/MS analysis was examined in order to explain the pathway of TZ biodegradation and it was suggested that hydroxylation, carbonylation, carboxylation, and ring cleavage were accrued and it was concluded that *Raoultella sp.* utilized TZ as the sole carbon and nitrogen source. The overall results demonstrated that the TZ biodegradation by *Raoultella sp.* could be great potential for the application in biological treatment of wastewater in practice (Liu et al., 2019).

In the study of Wu et al. (2019), co-metabolic enhancement of 1H-1,2,4-triazole (TZ), which is widely utilized as the main compound for the synthesis of triazole fungicides, biodegradation through nitrification was investigated in an activated sludge reactor. This removal method was chosen because the conventional biological process is quite unproductive for TZ removal due to highly intractable nature of TZ. The results showed the enhancement of removal of TZ, TOC, and dissolved organic matter thanks to the co-metabolic degradation of TZ in the continuous flow bioreactor. The major reason for the advanced removal performance was the enrichment of functional species related to nitrification and functional degrading species with the supplement of NH_4^+. GC/MS analysis was conducted for the identification of intermediates and five co-metabolic intermediates, including 2,4-dihydro-[1,2,4]triazol-3-one and [1,2,4]triazolidine-3,5-dione, were observed. The significant enhancement of microbial community in the co-metabolic system was proved via high-throughput sequencing analysis in the regard of richness, abundance and uniformity. This study has indicated that nitrification-assisted co-metabolism had a promising potential for the removal of intractable contaminants such as TZ from wastewater (Wu et al., 2019).

Wu et al. (2016) investigated biodegradation of 1H-1,2,4-triazole (TZ), which is broadly used in the production of insecticide, herbicide, fungicide, plant growth regulator and antitumor, antivirus and antibacterial agents, by a novel isolated strain *Shinella sp.* NJUST26. The isolation was properly done from TZ-contaminated soil and it was defined as *Shinella sp.*. The effects of pH (3.0-10), incubation temperature (20-40 ºC), initial TZ concentration (100-320 mg/L), and additional organic carbon source (0.5-2.0 g/L yeast extract, sucrose, glucose) was examined on the biodegradation of TZ. The optimum pH and temperature were determined as 6-7 and 30 ºC, respectively. The maximum volumetric degradation rate raised from 29.06 to 82.96 mg/L.d with increasing of initial TZ concentration from 100 to 320 mg/L, implying high tolerance of *Shinella sp.* NJUST26 towards TZ. The addition of yeast extract, sucrose, glucose at low concentration could be significantly enhanced the biodegradation of TZ by *Shinella sp.* NJUST26; however, the high concentration of additional organic carbon source negatively

affected the biodegradation. It was determined by GC/MS and HPLC/MS analysis that the main metabolites of 1,2-dihydro-3H-1,2,4-triazol-3-one (DHTO), semicarbazide, and urea formed during the TZ biodegradation. The pathway of the TZ biodegradation by *Shinella sp.* NJUST26 was as follows; TZ was firstly oxidized to DHTO, and then the cleavage of DHTO ring occurred to produce N-hydrazonomethyl-formamide, which could be further degraded to biodegradable semicarbazide and urea (Wu et al., 2016).

Satapute and Kaliwal (2016) assessed the ability of *Burkholderia* sp. strain BBK_9 for biodegradation of propiconazole (PCZ), which is a triazole foliar fungicide and used in agriculture. PCZ degrading bacterium BBK_9 strain was isolated from paddy soil and identified as *Burkholderia* sp. relying on the morphological characteristics and biochemical properties combined with 16S rRNA gene sequencing analysis. The effects of pH and temperature were investigated and the results showed that 8.89 μg/mL (89 %) PCZ was degraded at 30 $^{\circ}$C and pH 7.0 within 4 days. In the degradation process, PCZ acts as the sole carbon source and energy substrate, which can be used for the strain for its growth in mineral salt medium. The plasmid curing method using LD_{50} concentration was conducted in order to search the role of plasmid and in this method, three plasmids got cured in the sixth generation. Accordingly, 7.37 μg/mL PCZ could be degraded by the cured strain, indicating that there was no responsibility of the plasmid encoded gene for the PCZ biodegradation. On the other hand, it was observed that the plasmid cured cells were also a healthy competitor which has an ability to degrade the PCZ. The PCZ transformed into three important metabolites namely 1-(2,4-dich1orophenyl)-2-(1H-1,2,4-triazol-1-y1) ethanone, 1-[2-(4-chlorophenyl) ethyl]-1H- 1,2,4-triazole and 1-ethyl-1H-l,2,4-triazole during the bioconversion process. Consequently, the use of *Burkholderia* sp. strain BBK_9 for the biodegradation of PCZ is a good alternative in order to remove the contaminated pollutants providing toxic-free environment (Satapute & Kaliwal, 2016).

Photocatalytic Degradation

In the study of Lhomme et al. (2007), the degradation of cyproconazole, triazole fungicide used in agriculture, on foliage, and in cereal cultivation, by UV/TiO$_2$ photocatalysis in water using industrial TiO$_2$ coated non-woven paper. Irradiation was conducted in a cylindrical batch reactor in a thermostated tank at 25 $^{\circ}$C, fitted with a 25W low pressure fluorescent lamp placed vertically in a plugged tube. The described batch photoreactor was showed in Figure 4. The UV lamp was turned on to irradiate the solution including the fungicide after the adsorption equilibrium was achieved.
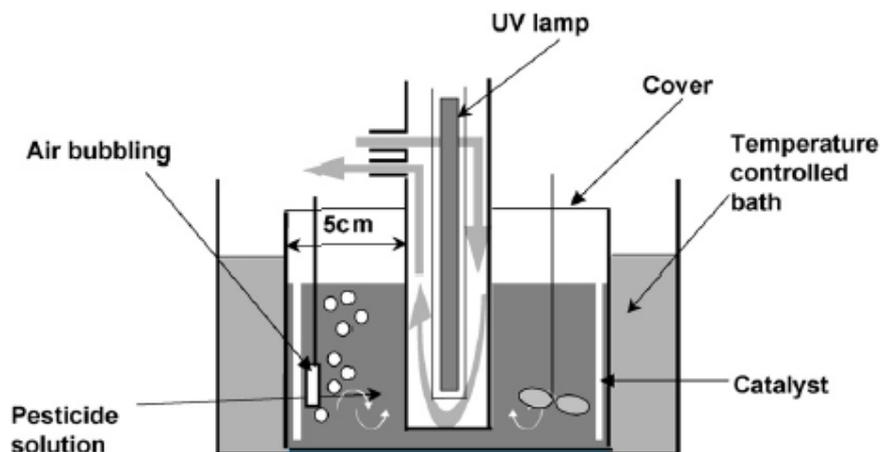
Figure 4. Batch photoreactor

The effects of dissolved oxygen on the degradation kinetics were investigated with and without air bubbling. Accordingly, even when the air bubbling was done for the forced oxygen transfer, approximately an 11% reduction in the oxygen concentration occurred. The original method considering account information obtained all along the course of the reaction for the calculation of the adsorption constant of the oxygen on TiO_2. It was determined that the calculated adsorption constant of the oxygen was quite close to the values of the degradation of cyproconazole and chlortoluron, approving the validation of the used original method. The first by-products as well as the final state of the pollutant's components such as the fate of carbon, chlorine and nitrogen were investigated. The analysis of the first by-products proposes that the hydroxyl radical attack takes place on the phenyl ring and methyl groups and on the carbon C1 of the cyproconazole before the opening of the aromatic ring. The findings of the fate of heteroatoms indicates that nitrate does not arise from ammonium oxidation, as the amount of NH_4^+ is constant, while the amount of NO_3^- increases. Ammonium and nitrate are formed differently from the nitrogen contained in triazole groups. The formation of N_2, cyanuric acid or other organic recalcitrant compounds could elucidate the lack of stoichiometric nitrogen amount. The chlorine atoms were entirely released as chloride ions. Overall result of this work indicates that TiO_2 coated on non-woven paper could be used as an efficient photocatalyst for degrading and mineralizing cyproconazole, and avoiding the toilsome filtration step, which limits the application of industrial photocatalyst process (Lhomme et al., 2007).

Zaza et al. (2001) have studied in the photodegradation of 3(5)-amino-1,2,4-triazole in aqueous solution by TiO_2 coupled to simulated sunlight. It has been known that the concentration of 3(5)-amino-1,2,4-triazole more than 0.1 μ/L causes potential pollution in surface and

groundwaters; therefore, it should be treated before discharging to receiving waters. The researchers suggest the UV plus semiconductor photocatalyst titanium dioxide as quite efficient tool for the removal of triazole herbicides in the final stages of water treatment. In this study, the irradiation was conducted with polychromatic light using heraeus apparatus equipped with xenon lamp having a spectral energy distribution similar to solar irradiation (> 290 nm). The maximum removal values of 3-amino-1,2,4-triazole in the presence of TiO_2 were achieved at pH 7.0 and the ratio 1/5 herbicide /TiO_2 (w/w). HPLC equipped with UV detector at 205 nm was used for the determination of the concentration of the remaining herbicide and metabolites. Accordingly, one metabolite was noticed and only 10% of this metabolite remained in the medium after 5 hours of irradiation. As a result, it is suggested that the photocatalysis by TiO_2 and solar light can be considered as a good alternative for the degradation of 3(5)-amino-1,2,4-triazole (Zaza et al., 2001).

In the study of Kuehr and Nunez (2007), the photocatalytic degradation of fungicide precursor of 1,2,4-triazole via TiO_2 and simulated solar radiation. A solar light simulator LS 1000W (Solar Light Co.) equipped with a xenon lamp and filters that reproduce solar UVB and UVA radiation (290–400 nm) were used. The mineralization was followed through chemical oxygen demand (COD) measurements at predetermined time intervals. The experiments were carried out at pH 8.0 because the degradation was not observed at lower pHs while the higher pHs enhanced the degradation rates. The degradation of 1,2,4-triazole progressed according to Langmuir–Hinshelwood mechanism. Accordingly, the adsorption equilibrium constants (K) and the rate constants (k) were found experimentally. As pKa increased, K values decreased while k values increased. Therefore, the rate constant related to the accessibility of the electron pair on nitrogen, but at the same time the electron pair repulsion induced by the negatively charged TiO_2 surface at pH=8.0 causes a converse effect in the adsorption equilibrium constant. These results showed that fungicides synthesized from triazole can be degraded at pH=8.0 using TiO_2 and simulated solar radiation (Kuehr & Núñez, 2007).

Electrochemical Oxidation

Han et al. (2014) have aimed to removal of triazole fungicides namely tricyclazole (TC), 1H-1,2,4-triazole (Tz) and propiconazole (PPC) via electrochemical oxidation using TiO_2-NTs/SnO_2-Sb/PbO_2 anode. Bulk electrolysis study was carried out and the results showed that the oxidation and mineralization reactions of three fungicides by HO• followed the pseudo first-order kinetic model. The oxidation rates indicated the following degradation sequence: PPC >

TC > Tz. Moreover, atom charge was calculated by semi-empirical DFT method and active sites of triazole fungicides were classified respectively. GC-MS and LC-MS/MS were used for the analysis of the intermediates. In brief, the calculation of active sites showed that N6 (0.406), N8 (0.279) and N9 (-0.303) were found to be active sites for TC and hydroxylation was first located at N8 position and then at N9 position. For Tz, the most abundant charge was observed at N5 (-0.494) and 2,4-Dichlorobenzoicacid-methylester was determined in the analysis. For PCC, it was found that C6 (0.312) was active site and the hydroxylation of C6 caused to the formation of the intermediates. Toxicity reduction of triazole fungicides solutions during the electrochemical oxidation process was evaluated and it was obtained that the acute toxicity of TC and PPC solution significantly decreased After treatment in the electrochemical oxidation reactor. Conclusively, the electrochemical oxidation method used in this study suggests a feasible and promising prospect for efficient removal of triazole fungicides from wastewaters (Han et al., 2014).

In the study of Urzua et al. (2013), the electrochemical oxidation treatment in water of three conazole fungicides, myclobutanil, triadimefon, and propiconazole, has been investigated at constant current using a boron doped diamond/stainless steel system (BDD/SS). Conazole fungicides include a triazole ring in their structure, a halogenated aromatic ring, and an alkyl chain or aliphatic heterorings and they generally used in clinical and agricultural applications. They can be evaluated for the protection of fruit, vegetable, and cereal crop as fungicides while they can be applied to treat local and systemic fungal and yeast infections in clinical purposes. For the treatment of the conazole fungicides, each solution were electrolyzed to evaluate the influence of the experimental parameters such as current, pH, and fungicide concentration on the removal of each compound and total organic carbon (TOC) reduction. Then, high performance liquid chromatography, ion chromatography and gas chromatography coupled with mass spectrometry were used for the analysis of the degradation by-products and suitable reaction pathways. Accordingly, the degradation of the conazole fungicides and their by-products is practically pH-independent and almost a complete removal of fungicides is obtained after 150–180 min. Almost complete mineralization with high efficiency was achieved at the current density of 50 mA/cm^2; also, this current density value is preferable due to the reasonable energy consumption. The pseudo first-order kinetic model was well-fitted to the electrochemical oxidation of three conazole fungicides and it was observed that the rate constants were proportional to the current in the range of 15–50 mA/cm^2, which was consistent with the raise of the adsorbed •OH at anode. Due to the parasite reactions, the rate constant

decreased at 80 mA/cm^2. According to the reaction pathways; aromatic intermediates, aliphatic carboxylic acids and Cl$^-$ were detected previous to their complete mineralization to CO_2 while NO_3^- anions remained in the treated solution. At the obtained conditions, almost total mineralization with 94–96% TOC removal of conazole fungicides was acquired through the electrochemical oxidation using BDD/SS, which provides a practical and applicable method for the treatment of wastewater containing conazole fungicides (Urzúa et al., 2013).

Cui et al. (2017) have aimed to achieve high level standard reuse of triazole fungicides discharged water via a novel integrated system in pilot plant scale of electrochemical oxidation, upflow biological aerated filter, and electrodialysis. A novel enhanced electrochemical oxidation reactor was designed and applied as pretreatment process in order to raise the removal efficiency and make easier the recycling of the polluted waters. The flow diagram of integrated treatment system was presented in Figure 5. The anode was made of macro-porous titanium membranes electrode coated with RuO_2, while tubular and fenestrated stainless steel was used as cathodes. Four cubic meters bio-ceramic goes through bio-film colonization for 30 days which the activated sludge used to make the film was obtained from the PACT reaction tank in the same wastewater treatment plant. In the electrodialysis system, the membrane stack consisting of 40 cell pairs, i.e., 40 AEMs and 41 CEMs assembled in total and a couple of electrodes made of titanium coated with ruthenium with aid of 1% sodium chloride aqueous solution as electrode rinsing solution were used.
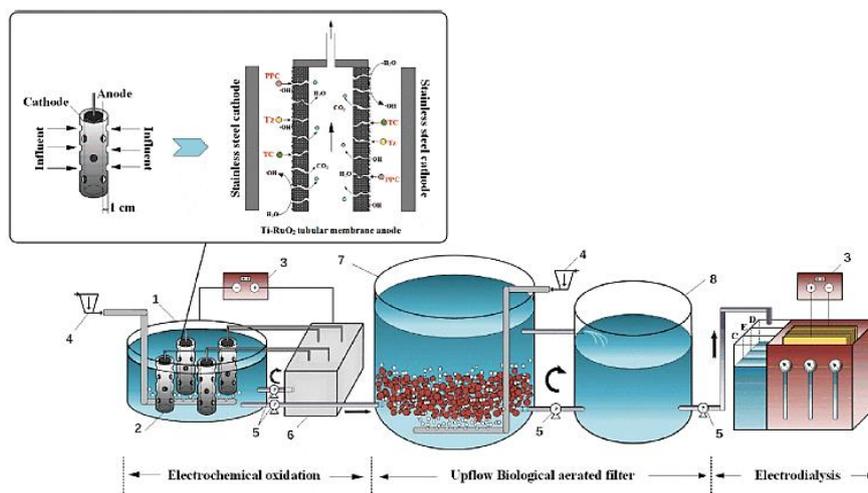
Figure 5. Flow diagram of integrated system for triazole fungicides discharged water advanced treatment (1) Electrochemical oxidation reaction tank, (2) electrode pair. (3) DC supply, (4) air compressor, (5) vertical centrifugal pump, (6) airtight stainless steel water tank, (7) upflow biological aerated filter, (8) balance tank. D: Dilute water compartment. E: Electrolyte Water Compartment. C: Concentrate water compartment

The effects of operating parameters were investigated with the discussion of economic evaluation and the optimum conditions were obtained as 5 mA/cm^2 current density, 3 m^3/h flow velocity, 5.0 pH value in the absence of supporting electrolyte. Over 90% removal from the discharged water containing the triazole fungicides was achieved at these conditions. It was thought that the remaining COD could be further raised from 250 mg/L to less than 60 mg/L thanks to the upflow biological aerated filter. Then, the electrodialysis provided the efficient removal of the salt. Lastly, a very low level of COD of 58.32 mg/L, TOC of 20.56 mg/L, $EC_{50,48h}$ of 73.1 ± 2.1%, consistent with an excellent removal of the target species of 94.19% tricyclazole, 90.11% 1H-1,2,4-triazole and 100% propiconazole, >99% salt and a low operating cost of $0.85 were achieved for the final effluent. These values meet the standard of high-level recycle for industrial water. Considering both the processing capacity and operating cost, it was concluded that this integrated system in pilot scale exhibits obvious flexibility and suitability in advanced treatment for chemical industry discharged water, especially for those with unbiodegradable organic contaminants and high salinity (Cui et al., 2017).

When the studies on the removal of 1,2,4-triazole fungicides from waters in the literature are evaluated, it has been seen that each method used has its own advantages and disadvantages. Based on these studies, the advantages and disadvantages of these methods are summarized in Table 5.

Table 5. Advantages and disadvantages of the methods used for the removal of 1,2,4-triazole fungicides from waters

Method	Adsorption	Degradation	Biodegradation	Photocatalytic Degradation	Electrochemical Oxidation
Advantages	✓ Low-cost ✓ Flexibility and simplicity of design ✓ Easy of operation	✓ Mineralization of the pollutants ✓ Rapid removal ✓ Efficient for recalcitrant molecules ✓ High reduction of chemical oxygen demand and total oxygen demand	✓ Economically attractive ✓ Efficiently elimination of biodegradable organic matters ✓ High removal of biological oxygen demand and suspended solids	✓ No production of sludge ✓ Usability of solar UV ✓ Strong light absorption of catalyst ✓ Mineralization of the pollutants ✓ No consumption of expensive oxidizing chemicals	✓ Less treatment time ✓ Less sludge production as compared to chemical and biological treatment ✓ Less land area as compared to biological process ✓ No need to add chemical for •OH formation due to generation it from water oxidation

Disadvantages	✖ Requirement of adsorbent regeneration ✖ Low selectivity ✖ Disposal problems for used adsorbents	✖ Lab scale ✖ Formation of by-productions ✖ pH-dependence ✖ Sludge production in some cases ✖ Usually work in batch mode	✖ Inefficient for non-degradable compounds or when toxic compounds are present ✖ Slow process ✖ Possible sludge bulking and foaming ✖ Generation of biological sludge and uncontrolled degradation products ✖ Complexity of biological mechanisms, so need to have good knowledge about enzymatic process	✖ Formation of by-products ✖ Lab scale ✖ Poisoning of catalyst by organic matters ✖ Low adsorption of organic pollutants ✖ Low quantum yield ✖ High cost for photo-source	✖ High operational cost due to high energy consumption (current density) ✖ Electrode fouling due to oxidation of pollutants on the electrode surface ✖ Requires post-treatment ✖ Technical constraints

Among these methods, it can be said that the less preferred and less efficient methods are biodegradation and photocatalytic degradation due to UV stability and poorly biodegradable nature of 1,2,4-triazole fungicides. Also, the elucidation of the biodegradation mechanisms of 1,2,4-triazole fungicides is still challenge; so, research on it continues. Recently, degradation, adsorption, and electrochemical oxidation processes have appeared as possible alternatives to traditional water treatment processes for the removal of 1,2,4-triazole fungicides. High removal efficiencies can be achieved by these methods; however, as can be seen in Table 5, they have some typical drawbacks in despite of their advantages. The removal method by gamma irradiation has come to the fore among recent studies because in this method, hydroxyl radicals can be formed more easily, sufficiently and cost-effectively, without the need for power supply or addition of chemicals under irradiation. In addition, as in the studies of Zendegi-Shiraz et al. (2021) and Cui et al. (2017) separately, high removal efficiencies can be achieved with the combined methods (adsorbent-catalyst coupling process and integrated system of electrochemical oxidation, upflow biological aerated filter, and electrodialysis), as well as high recyclable water quality. Consequently, further research and development in this area are required to overcome the shortcomings of the methods used for the removal of 1,2,4-triazole fungicides and to achieve high removal efficiency with the method to be developed.

The presence of 1,2,4-triazole fungicides in water is a major problem for the environment's conservation and health. The treatment processes of them are being investigated by several methods such as adsorption, degradation, biodegradation, photocatalytic degradation, electrochemical oxidation, and so on. Although each method has its own advantages, there are also disadvantages that limit their use in the industry. So, a combination of the methods is recommended to perform water treatment perfectly. After thorough analysis of wastewater containing 1,2,4-triazole fungicides, the highest removal efficiency and recyclable water quality can be achieved by using appropriate method combinations. However, the main problem is the application of these methods to a large scale. For this purpose, future research should focus on applying these methods to treat triazole fungicide-containing wastewater, first on a pilot scale and then on an industrial scale by means of more advances in water science and engineering as well as the assistance of multidisciplinary knowledge.

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