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Potential of *Cyperus alternifolius*, *Amaranthus retroflexus*, *Closia cristata* and *Bambusa vulgaris* to phytoremediate emerging contaminants and phytodesalination; Insight to floating beds technology

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ABSTRACT
The main aim of this study is to consider the potential of different aquatic and terrestrial plants (*Cyperus alternifolius*, *Amaranthus retroflexus*, *Closia cristata* and *Bambusa vulgaris*) for phytoremediation of pollutants and phytodesalination through floating bed system. In this study, when *Cyperus alternifolius* plants were exposed to atrazine (20 mg L^{-1}), OPC-LD (20 mg L^{-1}), OPC-LD (50 mg L^{-1}), fluorine (3.5 mg L^{-1}), and 1-4 Dioxane (25 mg L^{-1}), in a mesocosm treatment floating bed system, the phytoremediation efficiencies were 91.28 ± 6.35%, 82.33 ± 2.51 %, 75.67 ± 3.05%, 62.28 ± 5.77% and 42.29 ± 2.27 % respectively. When *Amaranthus retroflexus* plants were exposed to metformin (20 and 50 mg L^{-1}) and OCP-LD (20 and 50 mg L^{-1}), 63 ± 5.24 %, 58.4 ± 2.11%, 38 ± 1.73 %, and 29 ± 01 % of the pollutants were removed. In the case of *Closia cristata*, the most efficiency belonged to metformin with a concentration of 50 mg L^{-1}. The results showed that in water containing NaCl in a range of 1000 to 2000 mg L^{-1}, *Bambusa vulgaris* with an efficiency of about 32.62 ± 4.65 % is a good candidate for phytodesalination. Consequently, *C. alternifolius*, a fast-growing plant with a good ecological stability in polluted water, can absorb pollutants and remains healthy after the treatment period. It is a good candidate for phytoremediation in vegetated floating beds.

Keywords: Phytoremediation; Emerging Contaminant; Water pollution, *Cyperus alternifolius.*

INTRODUCTION
Inadequate sanitation provides pollution problems in developing countries (Starkl *et al.* 2018). Rivers are one of the main sources of drinking water all of the worlds and can be polluted by the human and industry activities. Rapid industrialization and lack of infrastructures in water treatment in developing countries have produced the point and nonpoint source pollutions (Gunawardena *et al*. 2018). Moreover, untreated wastewaters are commonly used for irrigation of crops in these countries. Wastewater irrigation has a potential risk for the health of human and ecosystem. There is a lack of knowledge regarding this kind of irrigation among farmers especially in aforementioned countries (Gunawardena *et al.* 2018). Moreover, water security, increasing crops yield and decreasing water costs are the main reasons for this unsustainable agriculture. Water, energy and cost-intensive technologies that usually are centralized, are ineffective in solving the complexity of water and wastewater treatment problems in developing countries (Zhang *et al*. 2014). Among different technologies for wastewater treatment, ecological technologies have gained more attention. Energy consumption, remediation efficiency, global warming potential, and wastewater treatment fees are important indicators that have been used for technology evaluation and selection (Su *et al.* 2019). Constructed floating wetlands (CFW), also called planted floating system beds, ecological floating beds, artificial floating islands and vegetated floating islands (Pavlineri, *et al.* 2017) which employ root system of vegetation by growing hydroponically and consequently, perform

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pollutant uptake from the water (Pavlineri *et al.* 2017). These floating systems have been widely used for the environmental remediation of eutrophic water in a cost-effective manner. This technology can be used effectively for the restoration of ecosystems and can remediate waters polluted by a variety of contaminants. In terms of engineering performance, ecological floating bed technology is stable, effective and reliable during the treatment period (Su *et al.* 2019). In indicators like global warming potential and eutrophication potential, this technology has shown superior performance. Energy consumption of constructed wetlands which is estimated between 0-0.25 kWh/m^3 (compared to 0.04 in stabilization ponds, 0 in rapid infiltration, 0.04 in slow rate infiltration, 0 in subsurface infiltration; 0 in overland flow; 0.31 in A_2 /O; 0.2 –0.3 in oxidation dishes; 0.28 in anoxic-oxic; 0.22-0.82 in conventional activated sludge; 4-23 in extended aeration; 0.23 – 0.31 sequence batch reactor; 0.2-0.6 in low-rate tricking filter; 0.5-1 in high-rate trickling filter and 0 in up-flow anaerobic sludge blanket reactor) is among low energy consumption technologies (Su *et al*. 2019). This technology can widely be applied to rural wastewater treatment, since it can integrate human society with the environment for improving the health of both human and the environment (Azizi *et al*. 2019). Emerging contaminants including industrial chemicals, pharmaceuticals, food additives, hormones, pesticides and herbicides are entered into the water by manufactural plants and agricultural runoff (Khalili Tanha *et al*. 2020). Atrazine) 2-chloro-4-ethylamino-6-isopropylamino-s-triazine) is used worldwide as atrazine herbicide for control of weeds in crop farmlands. It usually enters into the environment from agricultural production areas (Cao *et al.* 2018). Atrazine has long term adverse impact on environmental properties and is considered as an endocrine disruptor. It provides biotoxicity effects on human, animals, plants, and microorganisms (Lasserre *et al*. 2009). Removal of atrazine from agricultural runoff is necessary for keeping the ecosystem healthy and safe. In our previous study for identifying the efficiency of phytoremediation in the removal of atrazine from polluted water, *C. alternifolius* was used as floating beds in mesocosm-constructed wetland. Our findings revealed that when *C. alternifolius* were exposed to 20 mg L^{-1} atrazine, after a period of 20 days, 1.75 mg L^{-1} of this pollutant was remained in the solution (Asadi & Moogouei 2017). Dioxins, released to the environment as a byproducts of chlorine-based compounds, are considered as a most toxic chemicals in the environment (Kanan & Samara 2018). Dioxane can be accumulated in foods like eggs, dairy products, animal fats, and fish, hence finally in fatty tissues of fish and human. Because of persistence and toxicity, it exhibits a significant health risk to human. Dioxane has different sources in the environment. Industrial sources include pulp and paper, metal and chemical industries and also power boilers. Another important sources of emission of dioxane to the environment are diesel vehicles, coal-fired utilities, wood burning, and cement forges. Swedge sludge, municipal waste, medical waste, and hazardous waste through the incineration processes also release dioxane to the environment. Biochemical and photolytic processes, landfill burning and forest fire are also among reservoir sources of releasing dioxane to the environment. In our previous study, after exposure of *C. alternifolius* in floating beds to 25 mg L^{-1} 1-4 dioxane solution, 49.29% of dioxine was remediated after a period of 14 days and the plant was healthy after the treatment period (Bavarsad *et al*. 2018). Pharmaceutical products are stable chemicals and sometimes incompletely removed in wastewater treatments of plants (Oosterhuis *et al*. 2013). Ecotoxicity and residue potential of pharmaceutical products especially in rivers and marine ecosystems created public concerns in recent decades. They present in the environment in trace levels from ng L^{-1} to µg L^{-1}. However, environmental distribution and accumulation of these products have not been widely investigated. Pharmaceutical products like OPC-LD and metformin widely prescribe and use all over the world (Cui & Schröder 2016). In our previous study, when *A. retroflexus* and *Closia. cristata* were used in floating beds for phytoremediation of metformin, the remediation efficiencies reached 63% and 58.1% respectively (Moogouei *et al*. 2018). The metabolization of metformin in the human body is minor, so excrets unchanged in the urine (Oosterhuis *et al*. 2013). Metformin concentrations are reported in a range of 1.2-118 µg L^{-1} in wastewater treatment plants and 0.06-3.1 µg L^{-1} in surface water (Ghoshdastidar *et al.* 2015). When this plant was used for removal of OPC-LD, in 20 and 50 mg L^{-1}, the efficiencies of remediation were 82.33 % and 75.67 % respectively. Fluorine is a trace element related to human health. Excessive intake of fluorine causes damage to human soft tissues, bones, and teeth. Fluorine appears widely in the environment in the form of fluorite, cryolite, and apatite (Lu *et al.* 2016). Discharge of water, waste gases, and industrial wastes are among the main sources of fluorine pollution of the environment. In research on the potential of phytoremediation for fluorine removal in mesocosm constructed wetland, 62.28 % of fluorine was remediated from solution by *C. alternifolius* (Alijani *et al*.

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2019).Vegetative bioremediation of Na is a biological approach for phytodesalination. In soil pollution, under nonleaching condition, phytoremediation of salt is the only existing process for Na remediation (Rabhi *et al.* 2015). The area of lands degraded by salts, has been reported almost 2000 ha per day (Qadir *et al.* 2014). The main aim of the present study was to measure potential of different aquatic and terrestrial plants (C. *alternifolius, A. retroflexus, C. cristata, B.vulgaris*) in phytoremediation of atrazine, OPC-LD, fluorine and 1-4 Dioxane in floating beds as well as in phytodesalination.

MATERIALS AND METHODS

Plants Material

Based on literature, different plants were selected for phytoremediation in different geographical areas in Iran. These plants species should be able to grow in different environmental conditions. Moreover, local communities and companies should perform seed generation and growing plantlets. In this study, different plants species were used in two different conditions. At first, seeds were placed in floating beds and were fed by Hoagland medium. Therefter, adult plants were transferred to mesocosm-constructed wetland (Moogouei *et al.* 2011). Seeds were generated on the rafts then two-month hydroponically plants were transferred to the wetland for absorbing pollutants.

Design of mesocosm-floating beds

Rafts with a total surface area of 0.25 m^2 (50 cm × 50 cm) were used. 9 holes (3 cm in diameter) were designed in each polystyrene rafts. The thickness of the rafts was 2 cm, so the depth of the holes was 2 cm. The bottom surface of each raft was covered by mesh. Various-size seeds were settled on different size meshes. Rafts were placed on Hoagland medium and seeds were generated in each hole (Borghei *et al*. 2011). For increasing the stability of plantlets, the bottom of each hole was fully covered by seeds. In the case of transferring plant to the pilot, it was purchased, then anchored in wire rafts. Experiments were performed in room temperature (Average 25 °C) and natural light.

In this study, *C. alternifolius*, *A. retroflexus* and *C. cristata* were generated in floating beds for a period of 4 weeks. *Salicornia persica*, *Phragmites australis*, and *B. vulgaris* were transferred to the system from Neyzar district, Qom Province, Iran. Neyzar district is a rural area of Salafchegan city in Qom Province (34° 28′ 42″ N, 50° 27′ 25″ E) .The treatment period and solution concentrations were presented in Table1.

Table 1. Experimental condition for treatment and plants efficiencies.

Plant	Efficiency (%)	Pollutant	Initial concentration (mg L^{-1})	pH	Time (day)
C. alternifolius	91.28	Atrazine	20	5.5	16
	42.29	1-4 Dioxane	25	5.5	14
	82.33	OPC-LD	20	5.5	20
	75.67	OPC-LD	50	5.5	20
	62.28	Fluorine	3.5	5.5	14
A. retroflexus	63	Metformin	20	5.5	14
	58.4	Metformin	50	5.5	14
	38	OPC-LD	20	5.5	20
	29	OPC-LD	50	5.5	20
C. cristata	14.67	OPC-LD	20	5.5	20
	35	OPC-LD	50	5.5	20
	58	Metformin	20	5.5	14
	58.1	Metformin	50	5.5	14

Analysis of the water samples

After the treatment period, water samples in three replicates were obtained from each tray. Control samples were free of pollutant. The metformin, OCP-LD, and atrazine concentrations were assayed using High-Performance Liquid Chromatography) HPLC- Varian ProStar 210, Darmstadt, Germany). SPADNS spectrophotometry was

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used to assay fluorine concentrations in water samples. 1-4 dioxane was determined through mass spectrophotometry. During the treatment period, the pH of the solutions was adjusted to 5.5 and was measured with a portable pH meter. Salinity was measured using portable salinity tester.

Calculating efficiencies of remediation

Remediation efficiency (R%) was calculated using the following equation (Wang *et al*. 2018).

$$E = \frac{(C_0 - C_1)}{C_0} \times 100$$

Statistical Analysis

In this study, all the experiments were performed in triplicates and one sample was free of pollutant as control. Data were analyzed using Statistical Analysis System Origin 8 software package) OriginLab). Analysis of variance was applied to consider significance differences and Duncan test was used at $p<0.05$ to consider the mean comparison between data.

RESULTS

Phytoremediation of atrazine, 1-4 Dioxane, OPC-LD, and metformin from solutions

Data presented in Table 1 describes a mesocosm-field experiment with the time duration of treatment. Atrazine, 1-4 Dioxane, OPC-LD, and metformin are among common consuming chemicals and have anthropogenic impacts on the environment. In a period of less than 20 days, the main parts of these chemicals were removed from the water.

Phytodesalination of wastewater by *C. alternifolius, S. persica, P.australis,* and *B. vulgaris*

As shown in Table 2, the high NaCl concentrations in water were removed by *C. alternifolius, S. persica, P.australis,* and *B. vulgaris.* This range of salinity is usually more than freshwater ecosystems that were contaminated by salts. The periods of desalination were presented in Table 2.

Emerging contaminants and fluorine remediation efficiencies

As shown in Fig. 1, the most efficiency was obtained in the case of *C. alternifolius* when exposure to atrazine solution. *C. alternifolius* exhibited more potential for phytoremediation than *A. retroflexus* and *C. cristata.*

Phytodesalination efficiencies of plants

Fig. 2 depicts that *C. alternifolius* with the most remediation efficiency for these emerging contaminants did not absorb any NaCl. Phytodesalination efficiencies of *C. alternifolius*, *S. persica*, *P.australis* and *B. vulgaris* in different salinity condition were illustrated in Fig. 2. The experiments were carried out in 1 g L^{-1} NaCl solution as well as 1 and 2 g L^{-1} NaCl and KNO_3.

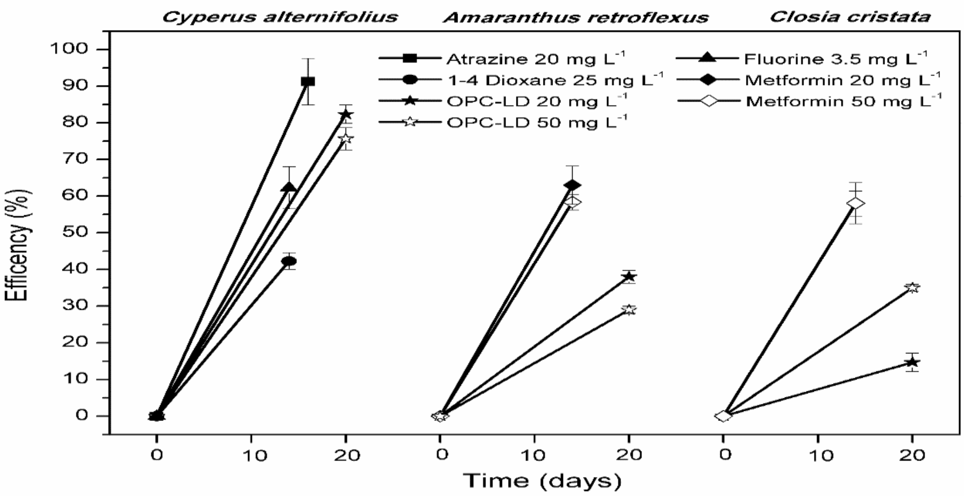

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Fig. 1. Remediation rate (%) of water contaminated with atrazine (20 mg l $^{-1}$), 1-4 Dioxane (25 mg L $^{-1}$), OPC-LD (20 mg L $^{-1}$) and fluorine (3.5 mg L $^{-1}$). All the data are means with three replicates ± SD. The significant level was considered as $p<0.05$.

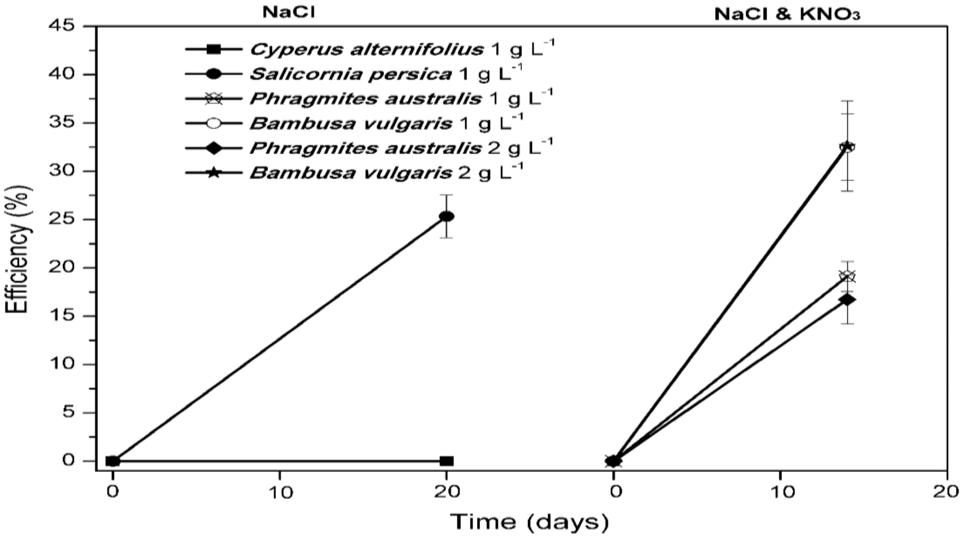

Fig. 2. Remediation rate (%) of water contaminated with high concentrations of NaCl (1 g L^{-1} NaCl as well as 1and 2 g L^{-1} NaCl and KNO_3). All the data are means of three replicates ± SD. $P<0.05$ data differences are significant.

Table 2. Experimental condition for phytodesalination studies and plant efficiencies.

Chemical	Efficiency (%)	plant species	Initial concentration (mgL^{-1})	Time (day)
NaCl	0	*C. alternifolius*	1000	20
	25.33	*S. persica*	1000	20
	19.12	*P. australis*	1000	14
	32.51	*B. vulgaris*	1000	14
NaCl & KNO_3	16.73	*P. australis*	2000	14
	32.62	*B. vulgaris*	2000	14

DISCUSSION

Floating beds as a naturally practical innovation, lately used to remove a variety of pollutants from the environment. When *C. alternifolius* was exposed to atrazine (20 mg L $^{-1}$), OPC-LD (20 mg L^{-1}), OPC-LD (50 mg L $^{-1}$), fluorine (3.5 mg L^{-1}), and 1-4 Dioxane solution (25 mg L^{-1}), the phytoremediation efficiencies were 91.28 ± 6.35%, 82.33% ± 2.51, 75.76 ± 3.05%, 62.28 ± 5.77 % and 42.29 ± 2.27% respectively. Potential of this plant for phytodesalination was zero. So, in the wastewaters, rivers, or other water bodies with no salinity, this species could be a potential candidate for designing and operating floating beds especially in agricultural areas with a high level of atrazine pollution in water. Tang et al. (2019) reported that the removal efficiency of *C. alternifolius* in a plant system for chlorpyrifos (a pesticide) at 50 - 500 µg L^{-1} was 94% - 98%. In the present study, when *A. retroflexus* was exposed to metformin (20 and 50 mg L^{-1}) and OCP-LD (20 and 50 mg L^{-1}), 63 ± 5.24 %, 58.4 ± 2.11%, 38 ± 1.73 %, and 29 ± 01 % of pollutants were removed from the solutions respectively. Potential of this species for phytoremediation of metformin was higher than OCP-LD. By elevating in the concentration of these pharmaceuticals, the potential of the plant for phytoremediation was decreased. In the case of *C. cristata*, the most efficiency was found against metformin at the concentration of 50 mg L^{-1}. In this study, 91.28% of atrazine (20 mg L $^{-1}$) was removed by *C. alternifolius* during 16 days. Cao *et al.* (2018) pointed out that phytostabilization of atrazine in soil may be one of the defense mechanisms of plants to pollution stress. However, this pollutant can be removed from the environment instead of stabilizing in the soil. In other words, the pollutants can be eliminated from the environment using floating beds, instead of stabilizing them in the soil. Cao *et al*. (2018) reported that when the atrazine concentration elevate from 0 to 30 mg L^{-1}, dissolved organic matters incorporate with atrazine and can produce strong bands. Phytoextraction as the mechanism employed in the present study, helps the soil

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and water environment to be remediated. In wastewaters with NaCl in a range from 1000 to 2000 mg L^{-1} , *B. vulgaris* with an efficiency of about 32.62 ± 4.65 % is a good candidate. In the study carried out by Robhi *et al.* (2015), *Suaeda salsa* absorbed 52.4% of soluble sodium from the soil. In addition, phytodesalination yield for *Sesuvium portulacastrum* was 26.0%. Besides, *Heliotropium curassavicum* reduced salinity by 26.5%.
The efficiency of phytodesalination by *Suaeda maritima* was 71.4%. Sodium adsorption capacity by *Suaeda maritima* and *Heliotropium curassavicum* were 80.8% and 48.7% respectively (Rabhi *et al.* 2015). In the present study, when *S. persica* exposed to 1000 ppm NaCl, phytodesalination yields were 25.33 ± 0.07 %. In a phytoremediation study for removal of metformin from aqueous solutions, after a period of 28 days, the removal efficiency of metformin by *Typha latifolia* was between 74.0 ± 4.1 % and 81.1 ± 3.3 % (Cui & Schröder 2016). However, in our study, metformin remediation efficiency was between 58± 3.42 % and 63 ± 5.24 %. The ability of floating beds to remove heavy metals from water has also been reported by some authors (Lin *et al.* 2019).

CONCLUSION

Phytoremediation studies are necessary for designing floating beds. These ecological floating beds are environmental friendly tools for enhancing water quality of water bodies especially rivers. *C. alternifolius* is a fast-growing species with good ecological stability in polluted water which can absorb pollutants and remain healthy after the treatment period, hence easily improving water quality. Our results revealed that the efficiency of *C. alternifolius* for designing a floating bed is significantly higher than *A. retroflexus*, *C. cristata*, *B. vulgaris,* while in the case of salinity of water or wastewater *C. alternifolius* can never be useful. The function of *A. retroflexus* and *C. cristata* in removal of pollutants was similar. Among aquatic plants, *C. alternifolius* can not tolerate salinity. Some of these pollutants are carcinogen, while there is no monitoring and remediation plan or act for them in aquatic ecosystems, hence increasing risks of the human and ecosystem health. Ecological floating beds are important tool for enhancing water quality and reducing risks of pollutant accumulation as well as endocrine disruption in the human and other living organisms. Moreover, our finding indicated that once phytodesalination, presence of nitrate ions in water elevates the phytoremediation potential. In the case of wastewater treatment, the ability of *B. vulgaris* for desalination in a high-salinity environment can be considered as a key point for the design of an ecological wastewater treatment system.

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بررسی توان سیپروس آلترنیفولیوس، آمارانتوس رتروفلکسوس، کلوزیا کریستاتا و بامبوزا وولگاریس برای پالایش آلودگی‌های نوظهور و شوری زدائی: چشم‌اندازی به تکنولوژی بسترهای شناور

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چکیده

هدف اصلی این مطالعه بررسی توان گونه‌های مختلف گیاهی آبزی و خشکی‌زی (سیپروس آلترنیفولیوس، آمارانتوس رتروفلکسوس، کلوزیا کریستاتا و بامبوزا وولگاریس) برای گیاه پالائی آلاینده‌ها و شوری‌زدائی از طریق سیستم بستر شناور است. در این مطالعه، وقتی سیپروس آلترنیفولیوس در معرض جذب آترازین (۲۰ میلی گرم بر لیتر)، OPC-LD (۲۰ میلی‌گرم بر لیتر)، OPC-LD (۵۰ میلی‌گرم بر لیتر)، فلوئور (۳/۵ میلی‌گرم بر لیتر) و ۱-۴ دی اکسین (۲۵ میلی‌گرم بر لیتر) دریک سیستم تصفیه بستر شناور متوسط قرار گرفت، کارائی گیاه پالائی به ترتیب ۶/۳۵ ± ۹۱/۲۸ ٪ ، ۲/۵۱ ± ۸۲/۳۳ ٪، ۳/۰۵ ± ۷۵/۶۷ ٪، ۵/۷۷ ± ۶۲/۲۸ ٪ و ۲/۲۷ ± ۴۲/۲۹ ٪ بود. هنگامی که آمارانتوس رتروفلکسوس در معرض جذب متفورمین (۲۰ و ۵۰ میلی‌گرم بر لیتر) و OCP-LD (۲۰ و ۵۰ میلی‌گرم بر لیتر) قرار گرفت به ترتیب، ۵/۲۴ ± ۶۳ ٪، ۲/۱۱ ± ۵۸/۰۴ ٪، ۱/۷۳ ± ۳۸ ٪ و ۰۱ ± ۲۹ ٪ آلاینده‌ها حذف شدند. بیشترین کارائی گیاه پالائی کلوزیا کریستاتا در جذب متفورمین با غلظت ۵۰ میلی‌گرم بر لیتر مشاهده شد. نتایج نشان داد برای شوری‌زدائی آب حاوی کلرید سدیم در غلظتی بین ۱۰۰۰ تا ۲۰۰۰ میلی گرم بر لیتر، بامبوزا وولگاریس با کارائی ۴/۶۵ ± ۳۲/۶۲ ٪ گزینه مناسبی است. سیپروس آلترنیفولیوس که گیاهی سریع الرشد و از نظر اکولوژیکی سازگار است در یک آب آلوده در طول مدت پالایش می‌تواند سالم بماند و در نتیجه گزینه مناسبی برای ایجاد بسترهای اکولوژیکی شناور تصفیه است.

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