Journal of Environmental Sciences Studies

Journal home page: www.jess.ir

Dechlorination of Zanjan Lead and Zinc Industry's Sewage using a Surface Flow Constructed Wetland

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Received: 02-02-2021
Accepted: 24-04-2021

Abstract

Environmental pollution is one of the concerns which affected human life and it is a must to find solutions for that. The effluent derived from the industrial units is contaminated with chloride. The amount of chloride in the effluent of studied lead and zinc industry is more than 50000 ppm and without an effective treatment system, will cause a lot of damage to the environment. Phytoremediation by Phragmites Australis plant has been used in a surface flow constructed wetland (CW) to reduce chloride concentration in the effluent. In the first pilot, the resistance of the plant to various chloride concentrations was measured. The sewage was tested with concentrations of 9250 and 4625 ppm. The results showed at these concentrations P.australis was able to reduce chloride concentration by 75.98% and by 92.33% respectively. In the second pilot, a CW on a laboratory scale was used to study the plant's behavior and chloride removal in a concentration of 2250 ppm. The plant performance was not satisfactory in this pilot and reduced the chloride concentration of the effluent by only 15.25%. These results indicate that P.australis has high efficiency in reducing chloride concentration and this yield is much higher in the summer season.

Keywords: Constructed Wetland, Dechlorination, Phytoremediation, Phragmites Australis, Wastewater treatment

Introduction

Nowadays treating wastewater to make it reusable has been a matter of debate in sustainable wastewater management practices globally. Effluents from urban and industrial activities can provide a wide range of chemical contaminants and microbial contaminants for water resources, especially surface water and groundwater (Murdock 1971). Wastewater sewages are lethal and this is because of hazardous by-products that had been produced during treatment procedures. This toxicity is also because of the compounds which are used to refine some instruments (Luo et al. 2014). Industrial wastewater is one of the most important environmental problems. Approximately in all industries, controlling the quality of the boiler feedwater is necessary for effective unit functioning. In this regard water softening is essential for ensuring the operation of boiler units because the existing calcium and magnesium in water leads to the hardness of the water over time and causes the formation of sediments and water pressure drop and gradually destroys the relevant facilities (Atkinson 2002; Dhodapkar et al. 2007; Masson and Deans 1996). Water softening is developed to eliminate hardness ions. The ion exchange method is the most widespread way of decreasing hardness in water, for its efficiency, easiness, recovery, selectivity, and a rather low cost (Gray 2000; Hoffmann and Martinola 1988; Klemes, Smith, and Kim 2008; Lazar et al. 2014; Zagorodni 2006). The ion exchange method is done by passing the sewage through a three-dimensional network to replace the calcium and magnesium bicarbonate ions (which are the cause of water hardness) with sodium ions. However, to reuse these ion exchange membranes, it is necessary to wash the membrane with sodium chloride solution so that the sodium ions are replaced by calcium and magnesium. This leads to the production of effluents with high concentrations of chloride ions that will be discharged into the environment and cause detrimental effects on it (Lazar et al. 2014). Chloride ions collect quickly during these processes accounted for massive amounts. Since the chloride is corrosive, it will damage the equipment through time (H. Liu et al. 2011). Another reason that makes dechlorination necessary is that chloride damages aquatic organisms and their ecosystems and it is toxic (White 2010). Dechlorination is a procedure through that the chloride is partly or mostly removed. The total chlorine residual in the wastewater should be around zero and this needs problematic necessities.

According to these necessities, water services tend to exert a great deal of chloride removal factors. These factors bring about important problems related to oxygen depletion and pH changes downstream of effluent disposal (Ryon et al. 2002). The available strategies for chloride ions elimination are variant. For instance: flocculent precipitation, ion exchange, using chemicals, membrane separation (Fleitlikh et al. 2017; W. Liu et al. 2018; Xiao et al. 2017). There are great weaknesses in existing methods of chloride removal from wastewater such as their costs and by-products. Hence, in this study, a new biological method is been examined which uses phytoremediation in a surface flow pilot-scale constructed wetland for dechlorination (Sagar et al. 2011). This study brings forward the plan of a CW[a] pilot plant for the treatment of chloride (Coppinietal.2019).The definition of Phytoremediation is to remediate polluted soil, sediments, and water by plants. This method is extremely environmentally friendly and it costs fewer prices in comparison with other available methods (McSorley et al. 2016). Based on the plants' capability and their endurance, different plants have been selected for this purpose. Capable plants not only endure various extent of contaminants, but they also keep a vast growth rate in polluted environments (Kushwaha et al. 2018). Several species of plants can be used in phytoremediation. According to their morphology, these plants are consist of three groups including free-floating such as Eichhornia crassipes, flooded like Myriophyllum sp. and emergent such as Phragmites australis and Typha domingensis (Valipour and Ahn 2016). During the last decades, the third group which is emergent plants are maximum used plants in CWs, especially P. australis is the most common one (Zhang et al. 2010). Phragmites australis (common reed) which is extensively distributed globally, is an emergent plant. Since the 1970s, Phragmites australis has been utilized for phytoremediation of several sorts of wastewater, soil, and sediments. According to the previous studies, it is proved that this plant accumulates high amounts of pollutants from contaminated water and soil (Rezania et al. 2019). The purpose of (Manjate, Ramos, and Almeida 2020) study was to check possible interferences of polyethylene microbeads (mPE[b]) (intentionally produced MPs) in the phytoremediation of metals by using Phragmites australis. Under the results, this plant had great potential in accumulating Intended metals in their belowground tissues (reaching ca. 1 mg/g of Cu and ca. 70 µg/g of Cd in roots). (Al-Homaidan et al. 2020) Analyzed the potential of a macrophyte Phragmites australis to be used in the heavy metal-polluted wetlands' phytoremediation in Arabian Peninsula. They found that P. australis has a good performance and is a suitable plant to be used in the phytoremediation of heavy metal-polluted particularly Cd-, Zn-, Cu-, and Pb-contaminated wadis in the Arabian Peninsula. In the study of (Nagy et al. 2020) to optimizing the condensed molasses soluble (CMS) concentration for rhizofiltration, the heavy metal accumulation and translocation properties of root accumulator two plant species (sedge (Carex flacca) and common reed (Phragmites australis)) were assessed. Based on the CMS application results, a considerable increment in bioaccumulation was noticed in the case of every examined heavy metal (As, Cd, Cu, Pb, and Zn) at the end of the experiment. Although constructed wetlands are not natural, they perform naturally in treating wastewater (Maucieri et al. 2017). Constructed wetlands work in the reciprocity performance of wastewater, soil, plants, and microorganisms under special circumstances including solidarity of some elements such as chemical, biological and physical elements (Q Wang et al. 2018).

2. Materials and Methods

In the present study, the treated wastewater of industrial units with a high concentration of chloride was purified using constructed wetlands driven by a surface flow system. The experiments were carried out in two stages, the first of which was carried out using pots during the spring and summer seasons. The second stage was done using a pilot-scale CW and carried out during the summer and fall seasons. Common Reed (Phragmites australis) was planted in both systems and after adaptation of plant growth and system stability, input flow was continuously regulated and sampling was started. The results are discussed in the following sections. Sampling was done in 3 replicates and then the mean of these replications is shown in the results.

2.1. Presentation of the study site

The study has been done in two stages. Both stages have been done on the campus of Environment College which is located in Karaj, Iran, in the Middle East region. DMS latitude longitude coordinates for Karaj are 35°49'57.58"N, 50°59'29.58"E. The study area is characterized by a humid climate with storms and rainfall as well as snowfall.

2.2. Industrial wastewater used

Treated wastewater of a lead and zinc plant (Zanjan city, Iran) was used. Two effluent samples were obtained from the boiler unit output of lead and zinc industrial units with concentrations of 52000 ppm and 37000 ppm chloride ions. The wastewater also includes other pollutants like Pb, Zn, etc. but as this wastewater is treated, then the only pollutant which has exceeded the standard levels in this effluent was chloride.

2.3. Plant species used

Phragmites sp. is distributed in almost all types of temperatures in all continents, particularly in Europe and Asia (Vymazal 2013). While this grass is distributed in different parts of Australia, South America, and North America, the most domination of it is in Europe (Mykleby et al. 2016). A moist situation such as a wetland is suitable for the growth of P. australis (Meng et al. 2016). This plant has a strong

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[a] Constructed Wetland

[b] polyethylene microbeads

rhizome and lengthy growing duration. It is also extremely adaptable to climate situations. The ability of P. australis potency in front of various types of pollution is proved (X. X. X. Liu et al. 2012). The availability of nourishments such as NO_3^- and PO_4^{3-} will augment the growth pace of P. australis (Uddin and Robinson 2018).The biomass yield of P. australis is affected by soil pH, the accessibility of nitrogen, and the place in which wetland is located (Shuai et al. 2016). The regrowth rate of P. australis biomass is under the effect of the harvesting period. If the harvest of this grass happens regularly about three times annually, the arid substance output nitrogen amount will upsurge (Tanaka et al. 2016). Yet, this could have detrimental effects on plant growth in the subsequent years (Rezania et al. 2019; Tanaka et al. 2017).

2.4. Experimental Setup

Planted P. australis in the greenhouse of college was used and only healthy plant seedlings of uniform size and weight were selected (Figure 1). Plant samples were planted in pots. After planting, the plants were initially yellowed and sprouted again after two weeks of continuous irrigation (Figure 2).

2.4.1. The experiments designed in the first step

Plants were planted in the soil gathered from the campus. The soil was poured into the pots and the plant samples were planted there. Soil samples were transferred to Amut Azma Laboratory in Tehran city for soil classification and texture. The first stage aimed to determine the concentration of chloride that the plant can grow in that concentration. The duration of the first pilot was two months (15th May to 15th July). In the first pilot, 6 pots at 5 different concentrations were used for the experiments. The chloride concentration of these pots is as follows: Pot NO. 1 = 52000 ppm, pot NO. 2 = 27740 ppm, pot NO. 3 = 18500 ppm, pot NO. 4 = 9250 ppm and pot NO. 5 = 4625 ppm. Pot NO. 6 was the control unit and was filled with water. Also, 5 control pots were not planted and were filled with wastewater at five mentioned concentrations.

Fig.1. uniform size of P. australis before they were planted in pots

Fig.2. planted P. australis inside of two pots to detect the evaporated water

2.4.1.1. Materials and consumables in the first pilot

- Pots for planting P. australis in them
- Ruler, to measure the amount of evaporated water
- Test glass for sampling
- Beaker for adding evaporated water to pots

2.4.2. The experiments designed in the second step

The purpose of this step was A: To measure the chloride removal percentage and B: To evaluate the effect of temperature and pH on its removal. A laboratory-scale pilot was used containing two units (one unit for planting P. australis and one unit as a control unit), two reservoirs, two water pumps, and a power outlet (Figure 3). Dimensions of each pilot unit were as follows: 430cm long, 45cm wide, and 60cm high. The volume of the reservoirs used was 250 liters for each one and the water pumps used in this project were the SOBO WP-3500 water pump. CW was lined with 15 cm of the existing soil in the garden of the college as a substrate. Then, 18 plants were planted in the pilot. The predicted time for experiments was 2 months (15th August to 15th October). We also had a planted unit filled with water considered as a control unit.

Fig.3. A laboratory-scale pilot (the second pilot) containing two units (1.planted unit, 2. Control unit)

2.5. Sampling

After a commissioning period of the vegetation, the sewage treatment plant was monitored every week for 2 months. Sewage samples were taken every 7 days during the experiment. During the monitoring period, sewage samples were collected in sterilized glass bottles for physicochemical analyses. The samples were transported into the laboratory in an ice chest under temperatures of 4°C to preserve the integrity of the samples before analysis.

2.6. Analyses of methods

2.6.1. Chemicals and equipment used for titration

- Silver nitrate (99.5% purity)
- Potassium Chromate
- The required amount of effluent sample (10 ml for each analysis)
- Laboratory supplies for titration including ring stand, buret, test tube, bubble pipette, dropper, Erlenmeyer flask, graduated cylinder, balance, funnel, wash bottle, and beaker
- Whatman filter paper grade 42 and size 12.5 with a porosity of 20 microns for filtering wastewater samples

2.7. Chemical analyses of industrial wastewater and hloride measurement

Industrial wastewater chloride was measured using the Mohr titration method. Mohr method is under the standard Mohr method (4500 B-Cl-; Argentometric Method) and the pH of wastewater was measured using the pH meter WTW525 model. These analyses were performed to measure the initial chloride content of industrial effluent and the required effluent analyzes during the running of the first and second pilot.

$$Cl^- + Ag^+ \leftrightarrow AgCl \qquad .1$$

$$CrO_4{}^{2-} + 2Ag^+ \leftrightarrow Ag_2CrO_4 \qquad .2$$

The solubility of silver chloride is much lower than that of silver chromate, and therefore, in the Mohr method, as long as not all chloride ions are precipitated, silver chromate precipitate does not form. The endpoint of titration occurs when all chloride ions are precipitated. Then, excess silver ions react with the chromate ions of the indicator (potassium chromate), to create a reddish-brown precipitate of silver chromate (Ramsay et al. 1955). Silver nitrate solution should be kept away from the light because it decomposes in the light and remains stable if kept in proper conditions (Kolthoff, Kolthoff, and Harris 1946). Hydrometer analysis was performed according to the ASTM D422 method. The Liquid limit test was performed according to AASHTO T 89 Standard Method and the Plastic limit test was performed according to ASTM D4318 Standard Test Methods. Soil classification was performed according to the USCS method (ASTM D2487-11) and soil was classified according to the USDA method (ASTM D3282-09). The method used is following the Standard Method (Standard Method 4500-H + B, ASTM Method D1293-84 (90) / (A or B) and USEPA Method 150.1). At the end of the experiments, the fresh weight of roots, stems, leaves, and weight of the samples was determined according to the standard methods for the examination of water and wastewater (APHA 2005).

2.8. Statistical analyses

All statistical data analyses were performed using the IBM SPSS statistical package V. 26.0. The performance of the Constructed Wetlands (CWs) was based on the inflow and outflow concentrations and abatements. The differences between groups were subjected to Paired t-test with a 95% confidence interval and correlation tests were also performed to determine the correlation rate between the Cl concentrations and plant biomass. The statistical significance level and was set to P = 0.05.

3. **Results & Discussion**

3.1.Preparation of materials and samples for the first stage

The effluent concentration used in pots was obtained by diluting two effluent samples which were gathered from industrial plant outlets. The concentration of effluent NO.1 was 52000 ppm and we used this concentration as our 100% sample (pot NO. 1). The concentration of effluent NO. 2 was 37000 ppm and pots NO. 2 to 4 of different concentrations (75%, 50%, 25%, and 12.5%) were filled with this sample. The concentrations of pots were as follow: 100% (52000 ppm), 75% (27740 ppm), 50% (18500 ppm), 25% (9250 ppm) and 12.5% (4625 ppm).The results showed that at a high concentration of chloride (more than 9250 ppm), P. australis was not viable and dried (pots NO. 1 and 2 and 3 started to dry from the second week and pot NO. 4 started to dry from the third week but sprouted again in the fourth week). The pollution load that the plant tolerated at 9250 ppm concentration was 18500 mg.During the test period, some of the water evaporated from the pot due to evapotranspiration, causing the pot to lower its water level. The amount of water lost was measured with a ruler and added to the pot because this will not affect the total chloride concentration. According to the analyses, the concentration was stable before and after water addition.Due to the desired retention time, the pots were sampled weekly and the effluent sample was transferred to the laboratory immediately and its chloride level was measured and recorded using the titration method. The pH of the samples was also measured and recorded using a pH meter. For each concertation, the control pot was considered without planting P. australis in it. The results showed that chloride levels in these high concentrations will not noticeably reduce with exposure to air. The chloride concentration removal in the first pilot and the control pots are presented in Tables 1 and 2.

Table 1. Chloride concentration removal (mean ± standard deviation) and pH samples of the 9250 ppm concentration

Time	**The concentration of the control unit**	**the pH of the control unit**
week 1	9250±100	7±0.65
week 2	9176±120	7.01±071
week 3	9155±148	7.02±0.83
week 4	9154.3±129	7.02±0.76
week 5	9150±150	7.03±0.87
week 6	9148.67±128	7.02±0.64
week 7	9145±122	7.03±083
week8	9144±100	7.03±082
Time	the concentration of the treatment unit	the pH of the treatment unit
week 1	9250±100	7±0.65
week 2	7760±101	7.01±0.52
week 3	4220±120	7.02±0.79
week 4	2727.16±114	7.02±0.77
week 5	2605±106	7.03±0.86
week 6	2258±125	7.04±0.62
week 7	2220±105	7.04±0.58
week8	2220±102	7.04±0.86

Table 2. Chloride concentration removal (mean ± standard deviation) and pH samples of the 4625 ppm concentration

Time	**the concentration of the control unit**	**the pH of the control unit**
week 1	4625±100	7±0.23
week 2	4610±101	7±0.72
week 3	4600±100	7.01±0.59
week 4	4596±106	7.01±0.76
week 5	4590±108	7.02±0.82
week 6	4585±104	7.03±0.55
week 7	4580±111	7.04±0.73
week 8	4580±110	7.04±0.76
Time	The concentration of the treatment unit	the pH of the treatment unit
week 1	4625±100	7±0.23
week 2	2743.33±113	7.01±0.52
week 3	1840±105	7.02±0.58
week 4	906.33±40.86	7.01±0.66
week 5	544.33±35	7.02±0.8
week 6	382±21	7.04±0.68
week 7	353±30.5	7.05±0.67
week 8	352±31	7.04±0.9

3.2. Preparation of materials and samples for the second stage

The pilot used in the second phase consisted of two units, P. australis was planted in one of them and one unit was considered as an unplanted control unit. A reservoir was installed upstream of each unit to maintain an effluent flow between the reservoirs and the units. At the outlet of the units at the bottom of the canal, the effluent returned to the tank using a water pump and it flowed between the tank and the pilot. The chloride concentration of effluent used in the second pilot was calculated according to the chloride concentration of the first pilot (18800 mg of pollutants).In the second pilot, sampling was carried out each week according to the desired retention time and the effluent sample was transferred to the laboratory immediately and its chloride was measured and recorded using the titration method. The pH of the samples was also measured and recorded using a pH meter. Results of the second pilot experiment presented in Table 3.

Table 3. Chloride concentration removal (mean ± standard deviation) and pH samples of the 2250 ppm concentration

Time	**the concentration of the control unit**	**the pH of the control unit**
week 1	2250±110	7.5±0.5
week 2	2247±103	7.5±0.8
week 3	2247±103	7.56±0.7
week 4	2246±108	7.61±0.9
week 5	2245±109	7.68±0.8
week 6	2244±102	7.73±0.7
week 7	2244±109	7.81±0.4
week 8	2244±92	7.99±0.4
Time	the concentration of the treatment unit	the pH of the treatment unit
week 1	2250±110	7.5±0.5
week 2	2133±144	7.52±0.8
week 3	2063±119	7.6±0.8
week 4	1956±135	7.68±0.9
week 5	1916±125	7.74±0.8
week 6	1913±140	7.82±0.75
week 7	1907±171	7.9±0.5
week 8	1906±140	8.06±0.6

3.3. Interpret the results of chloride analyses

Based on tables 1 and 2 concentration of chloride in 9250 ppm chloride concentration decreased by 75.98% and in 4625 ppm chloride concentration, it decreased by 92.33%. This indicates that under appropriate temperature conditions, P. australis has performed acceptably.No decrease in chloride content in control pots not only indicates the effective role of P. australis in reducing chloride concentration in the first pilot, but it also showed that exposure to air had no significant role in reducing chloride content in high concentrations.

In the second pilot, chloride removal was low due to oxygen depletion and a decrease in temperature and also increasing of pH so the effect of temperature on chloride was quite evident, and with increasing and decreasing temperature, the reduction efficiency of this parameter also placed low and high.A paired t-test in SPSS was used to compare the performance of pilots containing plants with control ones. According to the results, a Paired t-test showed a significant difference between the concentration of control and the treatment for both concentrations (9250 and 4625ppm). For 9250ppm the data are as follows: P<0.001, df =7, t=5.125, and for 4625ppm the data are as follows: P<0.005, df=7, t=5.796 This may indicate the effective role of the plant in reducing the chloride concentration.

Table 3 shows the removal of chloride concentration in the second pilot. The rate of chloride removal in the planted unit containing 2250 ppm chloride, was 15.25% and no significant chloride removal was observed in the control unit and as mentioned in the results of the first pilot analyses, the lack of chloride removal in the control unit indicates the effective role of P. australis in dechlorination.The paired t-test in SPSS was subjected to compare the performance of pilots containing plants with control ones. According to the results, a Paired t-test showed a significant difference (P<0.001, df=7, t=5.282) between the concentration of control and the treatment. This may indicate the effective role of the plant in reducing the concentration. There was no significant difference between the reduction percentages in control units (P>0.05) and there was a significant difference between the reduction percentages between three treatment units (9250, 4625, and 2250 ppm) (P<0.05).

There was also a significant difference between the reduction percentages between control and treatment units in three concentrations (P = 0.47 for 9250 ppm, P = 0.006 for 4625 ppm, and P = 0.37 for 2250 ppm). According to Fig.4 that indicates the cumulative reduction percentages P. australis had a much better removal procedure in the first pilot than in the second one. This may indicate the effect of temperature on the process. In the first pilot, when the temperature was favorable, the P. australis was able to noticeably remove chloride concentration, but in the second pilot, the chloride removal rate was extremely reduced due to lower temperatures and reduced oxygen supply to the root.The study of (L. P. Wang et al. 2017) showed that the amount of dechlorination will raise with temperature upsurge which is in line with the result of our study; in the first pilot, the chloride removal was extremely acceptable while in the second pilot with a big drop in temperature, the chloride removal was noticeably reduced.

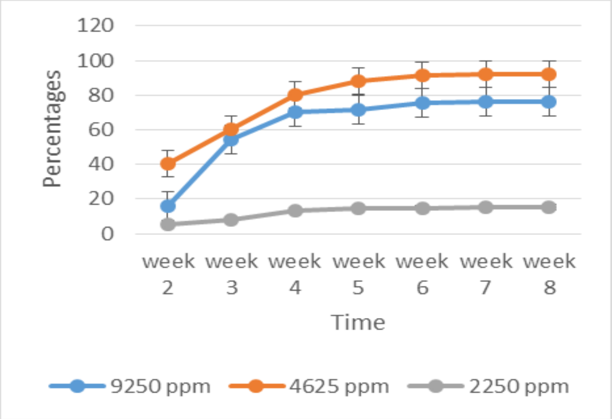


Fig.4 indicates the cumulative chloride reduction percentage

3.4. Analyses of pH

No significant change in pH was observed in the first pilot (Table 1). In the second pilot, the changing environmental conditions (decreasing temperature) resulted in an increase in pH and a decrease in chloride removal efficiency (Table 2).The range of pH changes in the first pilot in 9250 ppm sample was in the range of 7-7.03 and 4625 ppm sample was in the range of 7-7.04 and for the second pilot in the treatment unit, it was in the range of 7.5-8.06 and for the control unit, in the range of 7.5-7.99.According to (Patil and Paknikar 1999a; Sagar et al. 2011), the pH of wastewater affects the biosorption procedure. In this project, the maximum pH at which maximum biosorption occurred for the first pilot was 7.02 and the second pilot was 7.5. This can be a helpful result for the following similar researches as it demonstrates the suitable pH range at which the highest chloride removal happened (Patil and Paknikar 1999b; Sagar et al. 2011). Moreover, this range for the pH (7.0–7.5) was the most appropriate pH range for the activity of microorganisms that provide better conditions for the biosorption procedure (Guardia-Puebla et al. 2019). The pH values of wastewater for both units in planted and unplanted cells increased during the study period which is similar to the result of (Angassa et al. 2019) study. Analyses and studies have shown that decreasing temperature has a reverse relationship with increasing pH and decreasing temperature leads to an increase in pH, which is in line with the results of (Shahi et al. 2012).The correlation test between pH and concentration for the three treatment units (9250, 4625, and 2250 ppm) showed a negative correlation between them which means that with decreasing the concentration the pH will rise. Correlation for the 9250 ppm was significant at 0.01 level (P=0.002, N=8, r= -0.911) and for the 4625 and 2250 ppm was significant at 0.05 level (P=0.024, N=8, r= -0.776 for 4625 ppm and P=0.010, N=8, r=-0.834 for 2250 ppm). All of these three correlations were in a very strong range (0.8-1).

3.5. Biomass analyses

Fig.5 and Fig.6 show the trend of the measurements of plant biomass. The amount of dry and fresh biomass was affected by the chloride concentration. In this regard, the high the chloride concentration the low the biomass yield. The correlation test for concentration and fresh matter biomass was not done because some of the plants had been dried during the study period and their fresh matter biomass was not available. There was a significant negative correlation between the concentration and dry matter biomass (P=0.043<0.05, N=12, r= -0.825) which means the dry matter biomass decreased with increasing of the concentration.

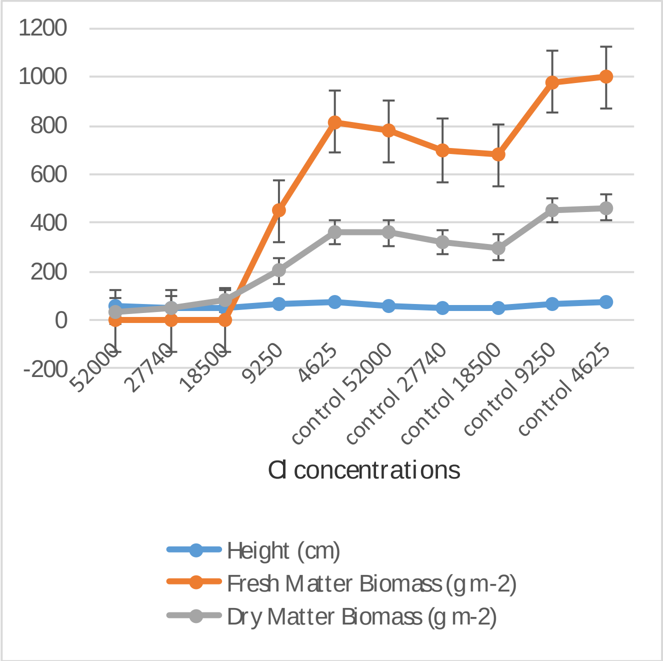


Fig.5 Fresh matter and dry matter biomass of the first pilot

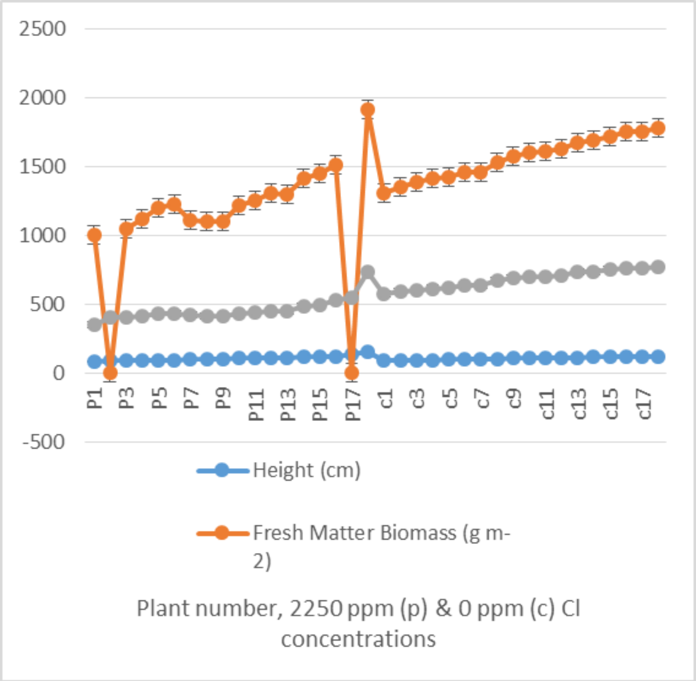


Fig.6 Fresh matter and dry matter biomass of the second pilot

Since there was only one specific concentration (2250) in the second pilot, we used a different kind of SPSS test for evaluating the biomass results of this pilot. There were significant differences between concentration level and dry matter biomass for both control and treatment units ($P<0.05$) at 95% confidence interval of the difference according to paired t-test results and there were also significant differences between the dry matter yield of control and treatment units.

3.6. Soil analyses results

According to the calculations, the bed soil includes 12% gravel, 40.38% sand, and 47% clay. Hence, it was sandy clay (SC). Since the soil has a very high percentage of clay, the soil can be considered as fine-grained and according to the results of the hydrometric test, the grading curve was continuous (Fig.7). Calculation of Atterberg limits showed that the soil liquid limit was 38.03 and the plastic limit was 18.1 (Table 4). Classification of soil by USCS revealed that the soil was classified as silty sand. Soil classification by USDA showed that the soil used in this project was clay.

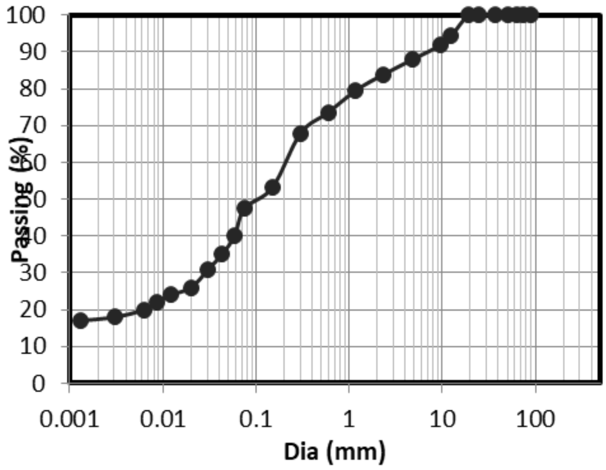
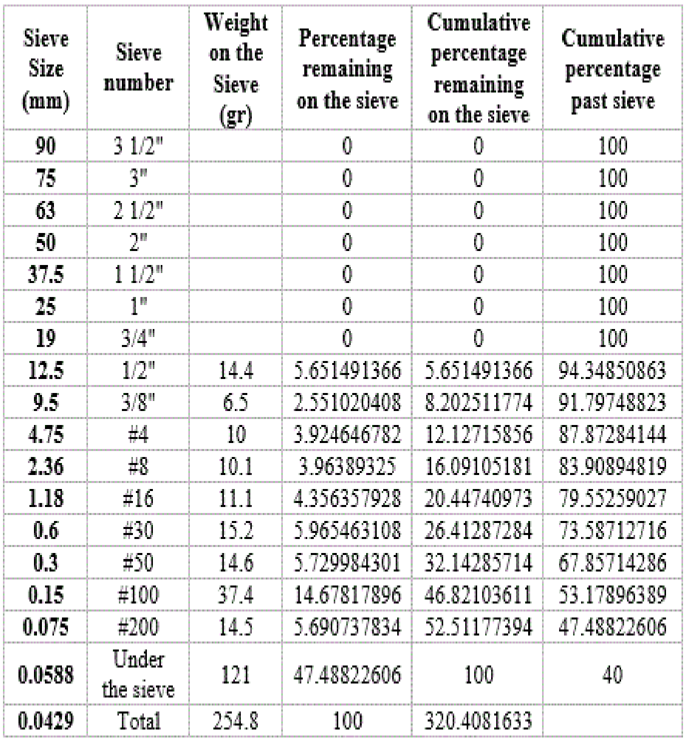


Fig.7 Litter Grading Curve

Table 4. Results of litter aggregate analysis



Sieve Size (mm)	Sieve number	Weight on the Sieve (gr)	Percentage remaining on the sieve	Cumulative percentage remaining on the sieve	Cumulative percentage past sieve
90	3 1/2"		0	0	100
75	3"		0	0	100
63	2 1/2"		0	0	100
50	2"		0	0	100
37.5	1 1/2"		0	0	100
25	1"		0	0	100
19	3/4"		0	0	100
12.5	1/2"	14.4	5.651491366	5.651491366	94.34850863
9.5	3/8"	6.5	2.551020408	8.202511774	91.79748823
4.75	#4	10	3.924646782	12.12715856	87.87284144
2.36	#8	10.1	3.96389325	16.09105181	83.90894819
1.18	#16	11.1	4.356357928	20.44740973	79.55259027
0.6	#30	15.2	5.965463108	26.41287284	73.58712716
0.3	#50	14.6	5.729984301	32.14285714	67.85714286
0.15	#100	37.4	14.67817896	46.82103611	53.17896389
0.075	#200	14.5	5.690737834	52.51177394	47.48822606
0.0588	Under the sieve	121	47.48822606	100	40
0.0429	Total	254.8	100	320.4081633	

4. Conclusions

Chlorides in water and wastewater are thoughtful anxiety in the time of water management and reuse. Wastewater should be chlorinated before being discharged to the natural environment considering the toxicity to aquatic organisms and the environment. The formation of chlorinated organic compounds is significant and during wastewater treatment processes these compounds do not remove. Dechlorination aims to remove the toxicity arising from chloramines, coming up from the reaction between chlorine with organic amines. Frequent types of these materials exist while a few numbers of them have known. Hence, this is a necessity to know the other forms and their impacts either.Different methods that are low-cost and efficient such as biological methods that are economical and environmentally friendly are required. The above paper is an effort towards finding such a method. From the above paper, the following conclusions may be drawn. Constructed wetlands are one of the most suitable technologies for developing countries. Constructed wetlands have a high potential for reducing chloride from industrial wastewater at appropriate temperature conditions. P. australis had well growth in the Alborz province in summer and although the soil has changed and moved on several occasions, plant growth has not stopped until November. P. australis was not able to grow at a chloride concentration above 9250 ppm and was dried at a higher concentration. The pollutant amount at which P. australis was able to survive was 18800 mg and the plant dried at a higher rate. At low temperatures, P. australis was unable to reduce the chloride concentration due to decreased oxygenation to the root and increasing pH. So by changing the plant breed and making it resistant to climatic conditions and also keeping the pH stable better results can be obtained.

5. **Recommendations**

- Designs for these types of systems must be carefully handled because they are a difficult task due to the similarity of these systems to the natural conditions of their process control.
- Wastewater input to these systems must be pre-treated to achieve better results.
- The system needs to be insulated when the air temperature is below normal. This is done by increasing the substrate depth (with increasing cost) by increasing the surface insulation. The water level may be lowered in winter to form air insulation in the system by forming an ice layer.
- This method is similar to natural treatment methods and is suitable for the removal of chloride in hot and high temperatures, which can provide a dynamic and environmentally friendly alternative in comparison to mechanical methods or other available dechlorination methods and maintenance.

Acknowledgements
The authors would like to thank the College of Environment for their support of this study.

References

- Murdock, W. W. Environment: Resources, Pollution, and Society. 1971.
- Luo, Y.; Guo, W.; Ngo, H. H.; Nghiem, L. D.; Hai, F. I.; Zhang, J.; Liang, S.; Wang, X. C. A Review on the Occurrence of Micropollutants in the Aquatic Environment and Their Fate and Removal during Wastewater Treatment. Sci. Total Environ. 2014, 473, 619–641. https://doi.org/10.1016/j.scitotenv.2013.12.065.
- Masson, M.; Deans, G. Membrane Filtration and Reverse Osmosis Purification of Sewage: Secondary Effluent for Re-Use at Eraring Power Station. Desalination 1996, 106 (1–3), 11–15.
- Atkinson, S. International Solvent Extraction Conference Reviewed. Membr. Technol. 2002, 2002 (5), 9–11.
- Dhodapkar, R. S.; Pophali, G. R.; Nandy, T.; Devotta, S. Exploitation Results of Seven RO Plants for Recovery and Reuse of Treated Effluents in Textile Industries. Desalination 2007, 217 (1–3), 291–300.
- Lazar, L.; Bandrabur, B.; Tataru-Fărmuş, R.-E.; Drobotă, M.; Bulgariu, L.; Gutt, G. FTIR Analysis of Ion Exchange Resins with Application in Permanent Hard Water Softening. Environ. Eng. Manag. J. 2014, 13 (9).
- Zagorodni, A. A. Ion Exchange Materials: Properties and Applications; Elsevier, 2006.
- Klemes, J.; Smith, R.; Kim, J.-K. Handbook of Water and Energy Management in Food Processing; Elsevier, 2008.
- Hoffmann, H.; Martinola, F. Selective Resins and Special Processes for Softening Water and Solutions; A Review. React. Polym. Ion Exch. Sorbents 1988, 7 (2–3), 263–272.
- Gray, N. F. An Introduction for Environmental Scientists and Engineers. Water Technol. p 2000.
- Liu, H.; Wang, Y.-Y. Y.; Chai, L.-Y. Y.; Xiao, H.-J. J.; Pei, F.; Shu, Y.-D. De; Hui, L. I. U.; Wang, Y.-Y. Y.; Chai, L.-Y. Y.; Xiao, H.-J. J.; Fei, P. E. I.; Shu, Y.-D. De; Liu, H.; Wang, Y.-Y. Y.; Chai, L.-Y. Y.; Xiao, H.-J. J.; Pei, F.; Shu, Y.-D. De; Hui, L. I. U.; Wang, Y.-Y. Y.; Chai, L.-Y. Y.; Xiao, H.-J. J.; Fei, P. E. I.; Shu, Y.-D. De. Effect of Impurities in Recycling Water on Pb-Ag Anode Passivation in Zinc Electrowinning Process. Trans. Nonferrous Met. Soc. China 2011, 21 (7), 1665–1672. https://doi.org/10.1016/S1003-6326(11)60912-6.
- White, G. C. White’s Handbook of Chlorination and Alternative Disinfectants; Wiley, 2010.
- Ryon, M. G.; Stewart, A. J.; Kszos, L. A.; Phipps, T. L. Impacts on Streams from the Use of Sulfur-Based Compounds for Dechlorinating Industrial Effluents. Water. Air. Soil Pollut. 2002, 136 (1–4), 255–268.
- Liu, W.; Lü, L.; Lu, Y.; Hu, X.; Liang, B. Removal of Chloride from Simulated Acidic Wastewater in the Zinc Production. Chinese J. Chem. Eng. 2018, 27 (5), 1037–1043. https://doi.org/10.1016/j.cjche.2018.06.025.
- Fleitlikh, I. Y.; Grigorieva, N. A.; Nikiforova, L. K.; Logutenko, O. A. Purification of Zinc Sulfate Solutions from Chloride Using Extraction with Mixtures of a Trialkyl Phosphine Oxide and Organophosphorus Acids. Hydrometallurgy 2017, 169 (February 2016), 585–588. https://doi.org/10.1016/j.hydromet.2017.04.004.

- Xiao, H.-F. F.; Chen, Q.; Cheng, H.; Li, X.-M. M.; Qin, W.-M. M.; Chen, B.-S. S.; Xiao, D.; Zhang, W.-M. M. Selective Removal of Halides from Spent Zinc Sulfate Electrolyte by Diffusion Dialysis. J. Memb. Sci. 2017, 537, 111–118. https://doi.org/10.1016/j.memsci.2017.05.009.
- Sagar, A.; Apte, S. S.; Kore, V. S.; Kore, S. V; Apte Shruti, A. sagar; Sagar, A.; Apte, S. S.; Kore, V. S.; Kore, S. V; Apte, S. S.; Kore, V. S.; Kore, S. V; Sagar, A.; Apte, S. S.; Kore, V. S.; Kore, S. V. Chloride Removal from Wastewater by Biosorption with the Plant Biomass. Univers. J. Environ. Res. Technol. 2011, 1 (4), 416–422.
- Coppini, E.; Palli, L.; Antal, A.; Del Bubba, M.; Miceli, E.; Fani, R.; Fibbi, D. Design and Start-up of a Constructed Wetland as Tertiary Treatment for Landfill Leachates. Water Sci. Technol. 2019, 79 (1), 145–155.
- McSorley, K.; Rutter, A.; Cumming, R.; Zeeb, B. A. Phytoextraction of Chloride from a Cement Kiln Dust (CKD) Contaminated Landfill with Phragmites Australis. Waste Manag. 2016, 51, 111–118.
- Kushwaha, A.; Hans, N.; Kumar, S.; Rani, R. A Critical Review on Speciation, Mobilization and Toxicity of Lead in Soil-Microbe-Plant System and Bioremediation Strategies. Ecotoxicol. Environ. Saf. 2018, 147 (January 2017), 1035–1045. https://doi.org/10.1016/j.ecoenv.2017.09.049.
- Valipour, A.; Ahn, Y.-H. H. Constructed Wetlands as Sustainable Ecotechnologies in Decentralization Practices: A Review. Environ. Sci. Pollut. Res. 2016, 23 (1), 180–197. https://doi.org/10.1007/s11356-015-5713-y.
- Zhang, C.-B.; Wang, J.; Liu, W.-L.; Zhu, S.-X.; Ge, H.-L.; Chang, S. X.; Chang, J.; Ge, Y. Effects of Plant Diversity on Microbial Biomass and Community Metabolic Profiles in a Full-Scale Constructed Wetland. Ecol. Eng. 2010, 36 (1), 62–68.
- Rezania, S.; Park, J.; Rupani, P. F.; Darajeh, N.; Xu, X.; Shahrokhishahraki, R. Phytoremediation Potential and Control of Phragmites Australis as a Green Phytomass: An Overview. Environ. Sci. Pollut. Res. 2019, 26 (8), 7428–7441. https://doi.org/10.1007/s11356-019-04300-4.
- Manjate, E.; Ramos, S.; Almeida, C. M. R. Potential Interferences of Microplastics in the Phytoremediation of Cd and Cu by the Salt Marsh Plant Phragmites Australis. J. Environ. Chem. Eng. 2020, 8 (2), 103658.
- Al-Homaidan, A. A.; Al-Otaibi, T. G.; El-Sheikh, M. A.; Al-Ghanayem, A. A.; Ameen, F. Accumulation of Heavy Metals in a Macrophyte Phragmites Australis: Implications to Phytoremediation in the Arabian Peninsula Wadis. Environ. Monit. Assess. 2020, 192 (3), 1–10.
- Nagy, A.; Magyar, T.; Juhász, C.; Tamás, J. Phytoremediation of Acid Mine Drainage Using By-Product of Lysine Fermentation. Water Sci. Technol. 2020.
- Maucieri, C.; Barbera, A. C.; Vymazal, J.; Borin, M. A Review on the Main Affecting Factors of Greenhouse Gases Emission in Constructed Wetlands. Agric. For. Meteorol. 2017, 236, 175–193. https://doi.org/10.1016/j.agrformet.2017.01.006.
- Wang, Q.; Hu, Y.; Xie, H.; Yang, Z. Constructed Wetlands: A Review on the Role of Radial Oxygen Loss in the Rhizosphere by Macrophytes. Water 2018, 10 (6), 678. https://doi.org/10.3390/w10060678.
- Vymazal, J. Emergent Plants Used in Free Water Surface Constructed Wetlands: A Review. Ecol. Eng. 2013, 61, 582–592. https://doi.org/10.1016/j.ecoleng.2013.06.023.
- Mykleby, P. M.; Lenters, J. D.; Cutrell, G. J.; Herrman, K. S.; Istanbulluoglu, E.; Scott, D. T.; Twine, T. E.; Kucharik, C. J.; Awada, T.; Soylu, M. E.; Dong, B. Energy and Water Balance Response of a Vegetated Wetland to Herbicide Treatment of Invasive Phragmites Australis. J. Hydrol. 2016, 539, 290–303. https://doi.org/10.1016/j.jhydrol.2016.05.015.
- Meng, H.; Wang, X.; Tong, S.; Lu, X.; Hao, M.; An, Y.; Zhang, Z. Seed Germination Environments of Typha Latifolia and Phragmites Australis in Wetland Restoration. Ecol. Eng. 2016, 96, 194–199. https://doi.org/10.1016/j.ecoleng.2016.03.003.
- Liu, X. X. X.; Huang, S.; Tang, T.; Liu, X. X. X.; Scholz, M. Growth Characteristics and Nutrient Removal Capability of Plants in Subsurface Vertical Flow Constructed Wetlands. Ecol. Eng. 2012, 44, 189–198. https://doi.org/10.1016/j.ecoleng.2012.03.011.
- Uddin, M. N.; Robinson, R. W. Can Nutrient Enrichment Influence the Invasion of Phragmites Australis? Sci. Total Environ. 2018, 613, 1449–1459. https://doi.org/10.1016/j.scitotenv.2017.06.131.
- Shuai, W.; Chen, N.; Li, B.; Zhou, D.; Gao, J. Life Cycle Assessment of Common Reed (Phragmites Australis (Cav) Trin. Ex Steud) Cellulosic Bioethanol in Jiangsu Province, China. Biomass and Bioenergy 2016, 92, 40–47. https://doi.org/10.1016/j.biombioe.2016.06.002.
- Tanaka, T. S. T. T.; Irbis, C.; Kumagai, H.; Inamura, T. Timing of Harvest of Phragmites Australis (CAV.) Trin. Ex Steudel Affects Subsequent Canopy Structure and Nutritive Value of Roughage in Subtropical Highland. J. Environ. Manage. 2016, 166, 420–428. https://doi.org/10.1016/j.jenvman.2015.10.055.
- Tanaka, T. S. T. T.; Irbis, C.; Kumagai, H.; Wang, P.; Li, K.; Inamura, T. Effect of Phragmites Japonicus Harvest Frequency and Timing on Dry Matter Yield and Nutritive Value. J. Environ. Manage. 2017, 187, 436–443. https://doi.org/10.1016/j.jenvman.2016.11.008.
- Ramsay, J. A.; Brown, R. H. J.; Croghan, P. C.; Ramsay, B. Y. J. A.; Brown, R. H. J.; Croghan, P. C. Electrometric Titration of Chloride in Small Volumes. J. Exp. Biol. 1955, 32 (4), 822–829.
- Kolthoff, I. M.; Kolthoff, J. M.; Harris, W. E. Amperometric Titration of Mercaptans with Silver Nitrate Using the Rotating Platinum Electrode. Ind. Eng. Chem. Anal. Ed. 1946, 18 (3), 161–162. https://doi.org/10.1016/S0003-2670(01)93844-9.
- APHA, A. WPCF (2005) Standard Methods for the

Examination of Water and Wastewater. USA Washingt. DC, USA 2005.

- Wang, L. P.; Lee, W. H.; Tseng, S. M.; Cheng, T. W. Removal of Chloride Ions from an Aqueous Solution Containing a High Chloride Concentration through the Chemical Precipitation of Friedel's Salt. Mater. Trans. 2017, 59 (2), M2017273. https://doi.org/10.2320/matertrans.M2017273.
- Patil, Y. B.; Paknikar, K. M. Removal and Recovery of Metal Cyanides Using a Combination of Biosorption and Biodegradation Processes. Biotechnol. Lett. 1999, 21 (10), 913–919. https://doi.org/10.1023/A:1005550707798.
- Patil, Y. B.; Paknikar, K. M. Removal and Recovery of Metal Cyanides Using a Combination of Biosorption and Biodegradation Processes. Biotechnol. Lett. 1999, 21 (10), 913–919. https://doi.org/10.1023/A:1005550707798.
- Guardia-Puebla, Y.; Pérez-Quintero, F.; Rodríguez-Pérez, S.; Sánchez-Girón, V.; Llanes-Cedeño, E.; Rocha-Hoyos, J.; Peralta-Zurita, D. Effect of Hydraulic Loading Rate and Vegetation on Phytoremediation with Artificial Wetlands Associated to Natural Swimming Pools. J. water L. Dev. 2019, 40 (1), 39–51. https://doi.org/10.2478/jwld-2019-0004.
- Angassa, K.; Leta, S.; Mulat, W.; Kloos, H.; Meers, E. Evaluation of Pilot-Scale Constructed Wetlands with Phragmites Karka for Phytoremediation of Municipal Wastewater and Biomass Production in Ethiopia. Environ. Process. 2019, 6 (1), 65–84. https://doi.org/10.1007/s40710-019-00358-x.
- Shahi, D. H.; Ebrahimi, A.; Esalmi, H.; Ayatollahi, S.; Dashty, N. Efficiency of Straw Plants in Removal of Indicator Pathogens from Sub Surface Flow Constructed Wetlands of Municipal Wastewater in Yazd, Iran. J. Heal. Dev. 2012, 1 (2), 147–155.