# *Industrial Wastewater Treatment of Steel Plant by Combining Two Systems of Adsorption Column and Membrane Filtration of Reverse Osmosis*

Azadeh Kalateharabi [a*], Babak Akram [b], Ghazaleh Yousofizinsaz [c], Seyed Ahmad Mirbagheri [d]

[a*] Khaje Nasir Toosi University of Technology (KNT), Department of Civil Engineering, Master of Environmental Engineering (M.Sc.), Tehran, IRAN
[b] University of Birmingham, Department of Civil Engineering, Master of Water Resources Technology and Management (M.Sc.), Birmingham, United Kingdom
[c] Babol Noshirvani University of Technology, Department of Civil and Environmental Engineering, M.Sc., Babol, Mazandaran, IRAN
[d] Khaje Nasir Toosi University of Technology (KNT), Faculty of Civil Engineering, Professor, Doctor of Philosophy (Ph.D), No. 1346, Valiasr Street, Mirdamad Intersection, Tehran, IRAN

**Abstract**

Freshwater resources are limited and economically worthwhile with socio-economic and environmental impact. Due to the extension of cities, industrial extension, and population growth, environmental pollution has become noteworthy. Heavy metals are pollutants that are produced by the industrial factory. Therefore, wastewater should be purified and treated and then be returned to natural water circulation. In this research, the removal of heavy metal Zinc at high concentrations in steel plant and the performance of the integrated system including activated carbon adsorption column (as pretreatment) and reverse osmosis (RO) membrane system under different operating conditions are investigated. The variable parameters studied are pH (4.5, 6.5, 7, and 9), pressure (5, 7, 9, and 11 bar), and Zinc concentration (30, 50, 70 mg/l) to obtain Zinc removal efficiency, turbidity dissolved solids (TDS), electrocoagulation (EC), and turbidity (TU) at constant temperature and flow rate. The results show that the efficiency of the integrated system at 9 bar pressure and the pH of 7.5 is considered to be optimal in terms of water outlet quality. At optimal conditions, the removal efficiency recorded for TDS is 98.1%, 97.4% for EC, 100% for Zinc and the turbidity removal efficiency is 95.3%, which are desirable. Moreover, the efficiency of this system at a high concentration of Zinc is evaluated. According to the results, it can be seen that the integrated system is resistant to probable shocks, high concentration and has a desirable efficiency since the efficiencies of all parameters are almost above 90%.

**Nomenclature:**

| | |
|---|---|
| RO | Reverse Osmosis |
| TDS | Turbidity Dissolved Solids |
| EC | Electrocoagulation |
| TU | Turbidity |

**Keywords:**

Heavy Metal Zn, Membrane Filtration, Activated Carbon, Industrial Wastewater, Reverse Osmosis

## 1- Introduction

The term heavy or rare metals have specific meanings. In most cases, it refers to metals that have a specific gravity of more than 4.5 gr/cm$^3$ as well as toxicity and sustainable existence in the environment. For the last couple of years, heavy metals have been considered environmental pollutants. These metals contaminate water and soil and thus threaten their lives (Wuana and Okieimen 2011); (Chaudhury, Mishra et al. 2019); (Haydar, S et al. 2020) It is possible to identify these heavy metals in industrial wastewater. These elements include organic and inorganic substances which can be seen in industrial wastewater (Oubane, M et al. 2020). The steel industry often requires a reliable source of water consumption. Moreover, it may pose risks and threats to the environment during different processes of manufacturing (Niu. L et al. 2020); (Svetozarević, M et al. 2021). Therefore, measures should be taken to eliminate, reduce and control these pollutants within environmental standards. One ton of steel produced in India requires a total of 25 to 60 m$^3$ of water (Arias-Navarro, Villen-Guzman et al. 2019); (Mei .Tang et al. 2020); (Sirajuddin, Rathi et al. 2010). China is also the world's largest steel manufacturer, accounting for about 14% of industrial water used in the industry (Huang, Ling et al. 2011). Besides, each steel plant in Malaysia uses an average of about 18,000 m$^3$ of water per day. This amount is mainly used in steel production for cooling purposes (Beh, Chuah et al. 2012). These examples denote that the process of steel manufacturing is a water-dependent industry. Therefore, choosing the best method for treating its effluent is necessary for saving water resources. Although there are several ways for removing heavy metals such as electrolysis, coagulation, oxidation, ion exchange, and adsorption, there is still no accurate information on the removal of Zinc using membrane filtration (Babel and Kurniawan 2003); (Mohan and Pittman Jr 2006); (Murshid, S et al. 2020). Membrane filtration is the cutting-edge technology used all around the world particularly in developing countries due to the wastewater treatment in food, printing, and pharmaceutical industries applications in petro-chemicals (Zheng, Zhang et al. 2015); (Tan, Ooi et al. 2020). In general, membranes and membrane processes can be classified into four groups: ultrafiltration (UF), reverse osmosis (RO), Nano-filtration (NF), and electro-dialysis (ED) (Crini 2005); (Zagklis, Vavouraki et al. 2015); (Crini and Lichtfouse 2019); (Mamah, Goh et al. 2020); (Noguchi, Nakamura et al. 2018). Reverse osmosis (RO) is a method in which the effluent is treated by passing through a semi-permeable membrane. Recently, these systems have been investigated for the removal of heavy metals (Nejati, Mirbagheri et al. 2019); (Kong, Ma et al. 2020); (Shinde, Ukarde et al. 2020). Ultrafiltration and microfiltration are capable of removing soluble mineral compounds such as iron and Zinc. Adsorption and membrane filtration are the most frequently studied for the treatment of heavy metal wastewater. Adsorption by low-cost adsorbents and bio sorbents is recognized as an effective and economic method for low concentration heavy metal wastewater treatment. Moreover, membrane filtration technology can remove heavy metal ions with high efficiency (Stafiej and Pyrzynska 2007). Up to now, several studies have been carried out to investigate heavy metals removal from wastewater.

Al-Jlil and Alharbi investigated the concentration of heavy metals in sewage wastewater, which exceeded the crop production limit, RO and Adsorption process were compared. They found that the minimum efficiency of heavy metal ions was 88.89% and 87.92% for the adsorption process and RO method respectively. Moreover, the Saudi betonies clay used as an adsorbent material is considered to be more economical compared to the Ro method (Al-Jlil and Alharbi 2010).

Arora et al, studied RO membrane method for DE fluoridation of underground water at various solute concentrations. The results showed that this method was an efficient way due to DE fluoridation of potable water because it worked at very low pressure and also other inorganic pollutants could be removed as well as fluoride. Moreover, by increasing the pressure, the rejection rate increased. Also, higher flux and higher rejection could be obtained by increasing the flow rate. It was also seen that pH had a significant effect on the removal of fluoride due to the strong hydrogen bonding caused by the fluoride ion in acidic solution (Arora, Maheshwari et al. 2004).

Zagklis et al, focused on the removal of olive mill wastewater phenols by membrane Filtration and resin adsorption/desorption. Membrane filtration removed these waste materials through the isolation of phenolic compounds. Moreover, the reverse osmosis which included the low-molecular-weight compounds was treated by resin adsorption/desorption after a Nano-filtration. To recover phenols and separate them from carbohydrates, the nonionic such as XAD4, XAD16, and XAD7HP resins were utilized. These recovered phenolic compounds were concentrated through vacuum evaporation until they reached the concentration of 378 g/l in Gallic acid (Zagklis, Vavouraki et al. 2015).

Mohan et al, investigated Almond shell non-magnetic (ASAC) and magnetically activated carbons (MASAC) to remove trinitrophenol from water. They concluded that MASAC and ASAC performed better at low PH. Moreover, by increasing the temperature, the adsorption of TNP decreased for ASAC. While TNP adsorption increased for MASAC. These temperature dependences were not significant. Also, The Langmuir monolayer adsorption capacity was higher for ASAC and ASAC and MASAC obtained higher TNP adsorption capacities or compared to other activated carbons (Mohan, Sarswat et al. 2011).

Brahmi et al, experimentally investigated the ballasted electro-flocculation (BEF) process in which they use the aluminum (Al) electrodes to remove heavy metals such as cadmium and Zinc from industrial mining wastewater (MWW). To evaluate the interactions between current intensity, polymer dose, stirring speed, and electrodes number, the response surface methodology was applied. It was seen that by increasing the ratio of micro sand to PEI polymer dosage, the filterability improved. However, the quality of the settled water was highly influenced by the flow rate and the current density (Brahmi, Bouguerra et al. 2018).

Mirbagheri et al, studied removing the Fe, Zn, and Mn from steel making plant wastewater in which they use the reverse osmosis (RO) and Nano-filtration (NF) membranes method. They deduced that NF had an acceptable performance with high water flow. Moreover, NF was more economical compared to the RO method (Mirbagheri, Biglarijoo et al. 2016).

Nataraj et al, carried out research in which they use a hybrid Nano-filtration (NF) and reverse osmosis (RO) pilot plant to remove the color and contaminants of the distillery wastewater. High fluxes led to significant rejection in TDS, COD, potassium which denoted that membranes were not influenced by fouling during wastewater run. Also, the reclaimed water by these two methods could be reused for municipal or industrial purposes. Moreover, this hybrid process reduced both wastewater treatment costs and fresh water consumption by using a point-source approach (Nataraj, Hosamani et al. 2006).

Shinde et al, experimentally investigated RO membrane separation and Carbon Capture Reactor adsorption column to treat wastewater. The parameters studied were (COD), (TDS), and conductivity. To obtain COD reduction, they tested different hydrophilic, hydrophobic, and ion exchange resins. They concluded that phobic resin, with a maximum dynamic binding capacity of 0.0208 mg/l and 50.0 ± 0.4 % COD reduction had the highest performance. Moreover, by combining the CCR and the reverse osmosis (RO), the decrease in COD and TDs were 85.0 ± 2.5 % and 93.0 ± 0.5 % respectively without membrane fouling. Also, a hybrid approach of adsorption coupled with membrane separation could be considered as an efficient and economic method for wastewater treatment (Shinde, Ukarde et al. 2020).

Almojjly et al, studied the coagulation combined with sand filtration as a pre-treatment process to reduce ceramic membrane fouling. Test results showed that hybrid coagulation/sand filter –MF was the best way in removing oil. Moreover, optimal permeate flux was obtained by using this process due to a reduction of membrane fouling (Almojjly, Johnson et al. 2019).

Ahmadizadeh et al, carried out research in which they used halophilic microorganisms and forward osmosis (FO) membrane to remove organic pollutants from synthetic saline produced water in an osmotic membrane bioreactor. They found that the removal efficiency of the COD was 98% due to a high rejection of the FO membrane. Moreover, the PW volume was decreased by 30 % in the FO membrane. Also, two-thirds and 88 % of the COD and oil and grease were decreased in the OMBR (Ahmadizadeh, Shokrollahzadeh et al. 2020).

Since Ultra-filtration and microfiltration have lower efficiency compared to reverse Osmosis (Chaturvedi and Dave 2012), RO is applied in this study to remove Zinc, TDS, EC, and turbidity from a steel Plant wastewater. Moreover, previous studies have investigated manganese, iron, and Zinc rejection (Huang, Ling et al. 2011);(Al-Jlil and Alharbi 2010). However, a high concentration of these heavy metals applying both RO and adsorbent systems for a steel-making enterprise has not yet been considered (Huang, Ling et al. 2011); (Al-Jlil and Alharbi 2010). The main goal of this research is to consider the performance of integrated RO and adsorbent systems for a steel plant at a high concentration of Zn to remove the heavy metal Zinc and reduce TDS and EC. In this study, an adsorbent system is used as a pretreatment system before RO membrane filtration to increase the efficiency and improve the filtration. The two main properties of adsorbents are the high ratio of specific surface area to volume and the other one is the tendency to adsorb certain substances in the liquid phase, which causes high adsorption power. Metals can be removed by adsorption on activated carbon, aluminum oxides, silica, clays, synthetic materials such as zeolites and resins, and other materials (Tchobanoglous, Burton et al. 2003).

## 2- Materials and methods

In this study, simulated wastewater was applied to a combination of absorption column and RO membrane systems. The system optimization method is used for removing Zinc metal, TDS, EC and turbidity. Therefore, experiments are run at various pressures (5, 7, 9, and 11) bar at a constant value of pH (7.5). Then, at the optimal pressure, pH values vary from 4.5 to 9 mg/l. The caustic soda solution of sodium hydroxide is added to the synthetic wastewater to achieve the desired PH. Finally, at the optimal pressure and PH, the concentration of Zinc varies from 30 to 70 mg /l to observe the performance of the integrated system in high concentration removal. All tests have been carried out at a constant temperature and flow rate.

### 2-1- Simulated wastewater

In this study, the characteristics of steel making plant wastewater are obtained from the results of wastewater in Esfarayen, north Khorasan province in Iran. Moreover, the analysis is based on the wastewater treatment of the Esfarayen steel plant. The final wastewater is from the different units of the complex which is transferred to the central treatment system. This analysis is presented in Table 1. The chemicals used in this research are obtained from the German Merck factory. To manufacture artificial test samples, chemicals with desired concentration are added to the distilled water according to table 1 to obtain the desirable wastewater. It is worth mentioning that the wastewater temperature is 25.6. The concentration of Zinc and manganese, as shown in Table 1, are 29 mg/l and 2.2 mg/l, respectively, with the highest concentration being related to the heavy metal Zinc. According to table 1, all elements are according to the standard B values of Malaysia (Mirbagheri, Biglarijoo et al. 2016) except for Mn and Zn. Therefore, if only the concentration values of Mn and Zn are treated, there would be no threat to the environment. Moreover, the concentration values of BOD, COD, TSS must be refined to reach the minimum standard values (Beh, Chuah et al. 2012). In this study, due to the lack of reagents for measuring Mn and COD, only four parameters EC, TDS, TU, and high Zn concentration have been investigated.

**Table 1.** Characteristic of Steel Making Plant

| parameter | chemical | Before Treatment(mg/lit) | Standard B |
|---|---|---|---|
| pH | - | 7.1 | 5.50-9.00 |
| Temperature | - | 25.6℃ | 40.00 |
| $BOD_5$ | sugar | 64.3 | 50.00 |
| COD | Starch & sugar | 392 | 200.00 |
| TSS | Clay betonies | 401 | 100.00 |
| Aluminum | Aluminum chloride | 1.5 | 15.00 |
| Fluoride | Fluorescent | 1.8 | 5.00 |
| Copper | Copper(II) chloride | 0.12 | 1.00 |
| Manganese | Manganese(II) chloride | 2.2 | 1.00 |
| Iron | Iron nitrate | 3.2 | 5.00 |
| Zinc | Zinc nitrate | 29 | 2.00 |

## 2-2- Pilute

To conduct the tests, a pilute consisting of an absorption column is used as a pre-treatment and a reverse osmosis membrane system located in the Environmental Laboratory of Khajeh Nasir Toosi University of Technology (KNT), faculty of Civil Engineering is utilized. The absorption column includes layers of sand and Jacobi activated carbon obtained from Sweden. Activated carbon is a strong absorbent with high adsorption (Kumari, Alam et al. 2019) and does not dissolve in any known solvent, and one of the most prominent features of this substance is the optional removal of contaminants (Crini, Lichtfouse et al. 2019). When the organic matter in the wastewater is in surface contact with the activated carbon, one layer of molecules of this organic material accumulates on the carbon surface due to the force imbalance between the molecules. After absorbing these materials, the activated carbon decomposes the organic material in the wastewater. The process of absorption by activated carbon consists of the following steps:

1. Solids are absorbed by a Van der Waals force and a bond dipole moment to the outer carbon surfaces.

2. Solids may move into the cavities.

3. Solids are absorbed by the inner walls of activated carbon cavities (Beh, Chuah et al. 2012).

The specific weight of activated carbon granules and sand is 600 $kg/m^2$ and 1500 $kg/m^2$, respectively. Table 2 shows the grading properties of activated carbon adsorbent and sand. In this study, an adsorption column with a diameter of 25 cm and a height of 80 cm is used. As shown in Figure 1, the adsorption column is filled with sand and activated carbon layers. This column consists of a drainage layer at the bottom of the column, 4 layers of activated carbon and 3 layers of sand with a depth of 10 cm. As mentioned, the adsorption column system acts as a pre-treatment and enters the membrane system after the wastewater passes through it. The reverse osmosis membrane pilute is available in the laboratory of the Khajeh Nasir Toosi University of Technology and is washed to clean the membrane. However, these cartridges are purchased due to the clogging of activated carbon cartridges and microfiltration. The membrane used in this study is a polyamide Film-Tec BW30-4040 (Mirbagheri, Biglarijoo et al. 2016). The membrane is 40 inches (1.16 m) long and has a diameter of 3.9 inches (99 mm). The characteristics of the RO membrane are given in Table 3 (Mirbagheri, Biglarijoo et al. 2016). After pre-treatment, the wastewater enters a 100-liter tank and passes through a 1-micron filter to remove suspended solids. Then, it enters the microfiltration cartridge which is for RO pilutes to remove sand, silt and turbidity from the input solution. A schematic diagram of the membrane system is shown in Figure 2 (Mirbagheri, Biglarijoo et al. 2016). The maximum temperature of this cartridge is 52 $^{o}C$ which is not able to remove bacteria and viruses and thus enters the Granular activated carbon cartridge which is used for RO pilutes to remove taste, odor and chlorine from the input solution. The operating temperature of this cartridge is 4.4 to 51.6 degrees Celsius. Finally, the wastewater passes through the membrane to remove heavy metals and other parameters and is divided into two flows, concentrated and refined flows.

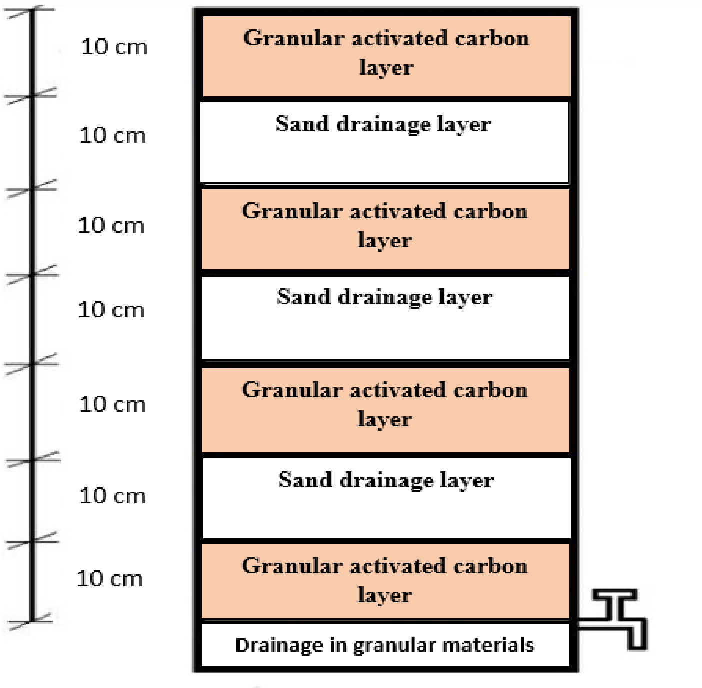


**Fig. 1.** Adsorption column (Pre-treatment)

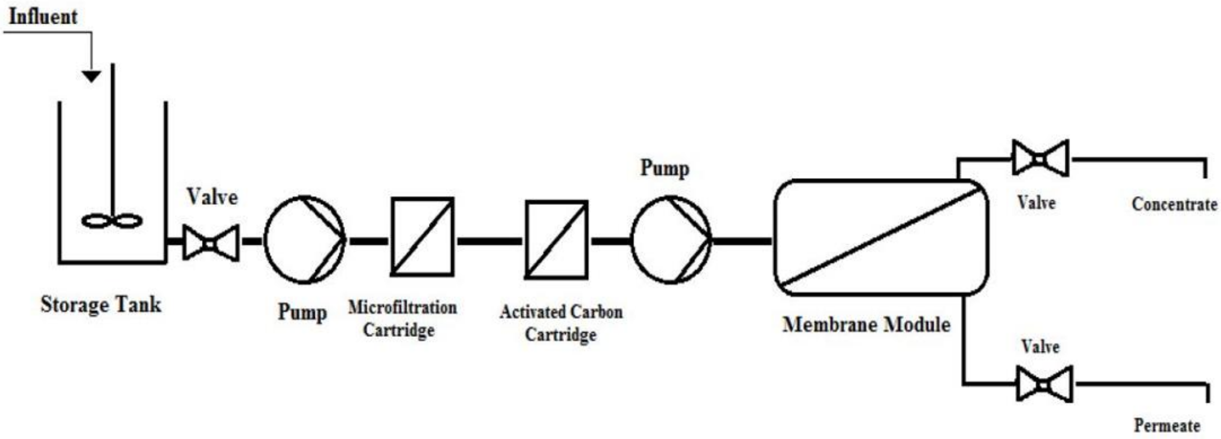


**Fig. 2.** Diagram of laboratory-scale reverse osmosis (Mirbagheri, Biglarijoo et al. 2016)

**Table 2.** The grading properties of activated carbon adsorbent and sand

| Mesh Number | Mesh Size | Activated Carbon Passage percentage | Sand Passage percentage |
|---|---|---|---|
| #4 | 4.75 | 100.0 | 100.0 |
| # 8 | 2.36 | 100.0 | 46.45 |
| # 16 | 1.18 | 26.7 | 30.28 |
| # 30 | 0.6 | 2.4 | 2.26 |
| # 50 | 0.3 | 1 | 0.67 |
| # 100 | 0.15 | 0.5 | 0.49 |
| # 200 | 0.075 | 0.0 | 0.0 |

**Table 3.** Characteristics of RO membrane (Mirbagheri, Biglarijoo et al. 2016)

| Product | Type | Active Area ($m^2$) | Maximum Operating Pressure | Maximum Operating Temperature | pH Range | Free Chlorine Tolerance |
|---|---|---|---|---|---|---|
| RO:BW 30-4040 | Polyamide Thin Film Composite | 7.2 | 41 bar | 45 ℃ | 2-11 | 0.1 ppm |

To measure the removal of heavy metals and compare them with each other, the term efficiency is used, which is shown as follows (Beh, Chuah et al. 2012):

$$E\ (\%) = [1- (C_P/C_O] \times 100 \qquad (1)$$

In equation 1, E (%) is the removal efficiency, $C_O$ is the initial concentration and $C_p$ is the concentration after purification. To remove Zinc, TDS, turbidity and EC in a combined adsorption column system and RO membrane system, the simulated wastewater of the steel industry is used. At the first step, the optimal pressure is obtained and at this pressure, the effect of pH on the removal efficiency of Zinc (as the highest concentration in wastewater), as well as TDS, turbidity and EC are studied. Then, at the optimal pH and pressure, the Zinc concentration varies from 30 to 70 mg /l to measure the efficiency of the integrated system. Finally, by comparing the efficiencies obtained from the integrated system, a suitable method is proposed for treating the wastewater of the steel unit.

## 3- Results and discussion

All tests are carried out at room temperature and parameters such as; time, volumetric flow rate and the other conditions remain constant. The storage tank volume is 100 liters (0.1 $m^3$). Moreover, the concentration and pH are controlled during the test.

### 3-1 - The effect of pressure on the removal efficiency

The pressures of 5, 7, 9 and 11 bar are applied to the wastewater. Changing the pressure at the natural constant pH of the effluent (pH = 7.5) can affect the wastewater flow rate and solute passage (Mohan, Sarswat et al. 2011) due to deprotonating of sorbent surface at moderate PH, which may lead to the reduction of the electro-static repulsion. After passing the wastewater through the integrated system and measuring the concentration of various parameters, the results are presented in Table 4. Then, by comparing the removal efficiencies, the pressure at which the highest removal efficiencies obtained is considered as the optimal pressure. The concentration of metal ions is also measured using a spectrometer. As can be seen from table 4 and figure 3 the removal efficiency of Zn is almost similar at all pressures, with removal efficiencies of 98.6 %, 98.2%, 100% and 100% for 5, 7, 9 and 11 bar respectively, which denotes that the applied pressure has no significant effect on removal efficiencies of Zn. This may be because the organic material deteriorates and the non-biodegradable membrane-rejected substances are enriched in the raw water during the test which is compatible with the previous study (Li, Chang et al. 2020). At a pressure of 11 bar, the removal efficiency of TDS and EC is lower than other pressures, which is due to concentration polarization followed by mass transport (Al-Rashdi, Johnson et al. 2013); (Mirbagheri, Biglarijoo et al. 2016). However, pressure 9 bar is considered to be the optimal pressure since the highest removal efficiency happens at this pressure.

**Table 4.** Effect of pressure on removal efficiencies at Constant pH

| Pressure (bar) | Tu (NTU) | CZn (mg/lit) | TDS (mg/lit) | EC (µmohs/cm) |
|---|---|---|---|---|
| 5 | 93.1 | 98.6 | 95.3 | 94.5 |
| 7 | 94.4 | 98.2 | 96.4 | 96.5 |
| 9 | 94.3 | 100 | 97.1 | 96.4 |
| 11 | 91.6 | 100 | 84.1 | 83.9 |

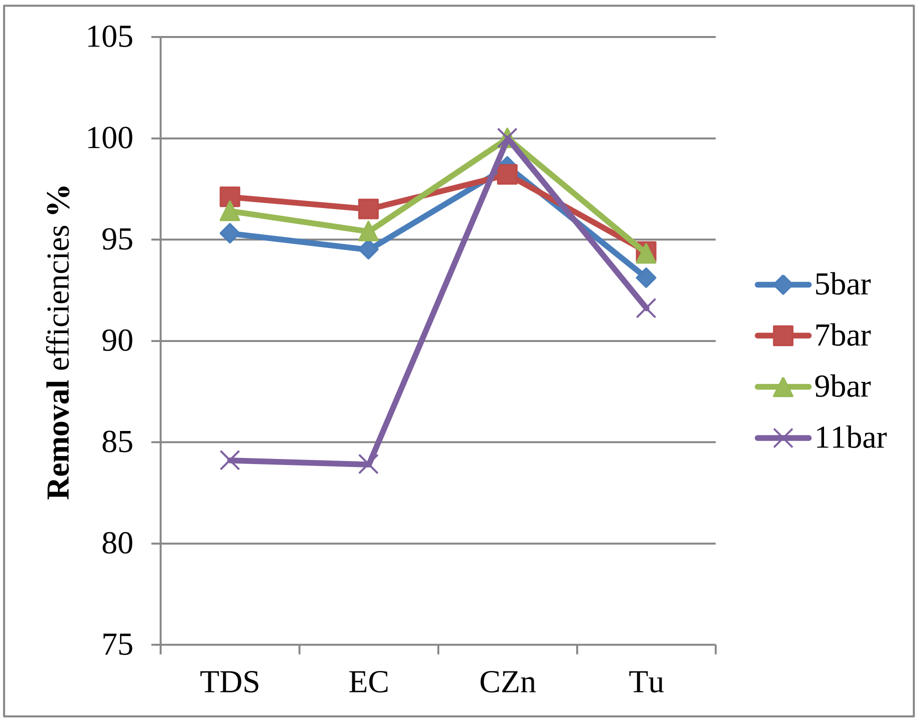


**Fig. 3**. Effect of pressure on the removal efficiencies at constant PH.

### 3-2 - The effect of pH on the removal efficiency

Since the uptake of solutes through the membrane can be affected by pH variation (Mohan, Sarswat et al. 2011), the pH level is measured by a calibrated pH meter. The optimal pH is achieved by comparing removal efficiencies at an optimal pressure of 9 bar and at a constant flow rate of 3 lit/min. The results are presented in Table 5. The removal efficiencies of Zinc in all tests are 100 which cannot be desired criteria for selecting PH. To achieve the optimal PH, the removal efficiencies of heavy metals for different pH values are drawn as shown in figure 4. A pH of 9 obtains the highest removal efficiency which denotes that as the pH value increases, the removal efficiency increases. This may be because the pH can change both the pore size and nature of the membrane surface charge and thus can influence the membrane separation by affecting the absorption capacity of the solutes and hydration on the membrane which is compatible with previous studies (Al-Rashdi, Johnson et al. 2013); (Arora, Maheshwari et al. 2004); (Mirbagheri, Biglarijoo et al. 2016). However, because at high pH values the Nano adsorbent's surface may be destroyed due to the hydroxylase complexes of the metal ions (Wadhawan, Jain et al. 2020). Therefore, the optimal pH of wastewater is close to 7.5, the point at which most of the diagrams have desirable removal efficiencies greater than 95% due to a high rejection of the RO (Ahmadizadeh, Shokrollahzadeh et al. 2020). This may be because of deprotonating of sorbent surface at moderate PH, which reduces the electro-static repulsion and therefore improve the rate of the adsorption (Wadhawan, Jain et al. 2020).

**Table 5.** Effect of pH on removal efficiencies at Optimum Pressure

| pH | Tu (NTU) | CZn (mg/lit) | TDS (mg/lit) | EC (μmohs/cm) |
|---|---|---|---|---|
| 4.5 | 91.1 | 99.8 | 83.1 | 81.9 |
| 6 | 94.2 | 100 | 92.3 | 90.8 |
| 7.5 | 95.3 | 100 | 98.1 | 97.4 |
| 9 | 100 | 100 | 100 | 98.9 |

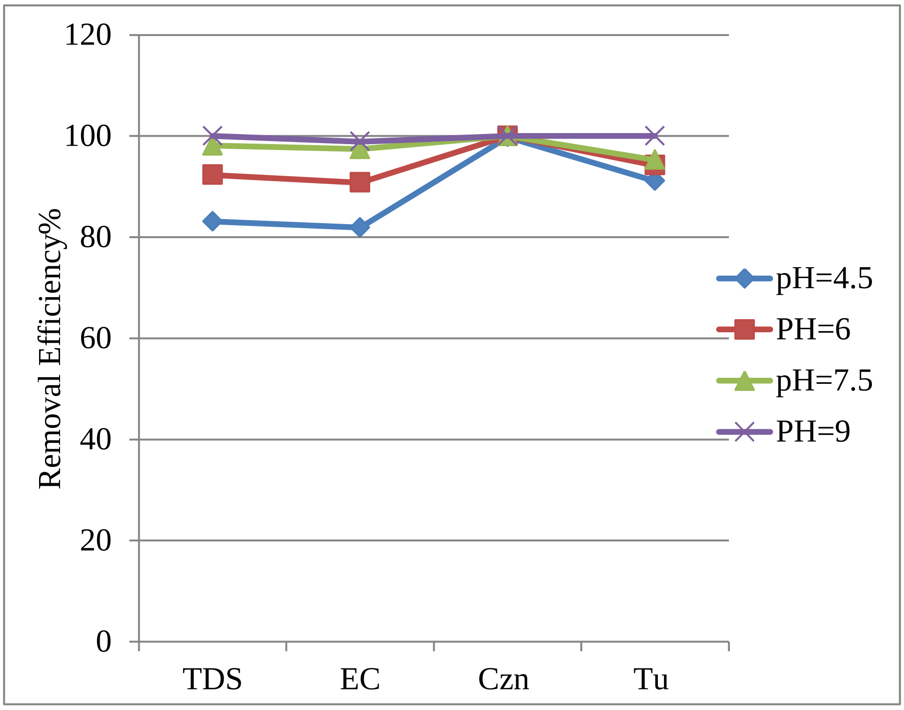


**Fig. 4.** Effect of pressure removal efficiencies at optimum pressure

### 3-3 - The effect of Zinc concentration on the removal efficiency

To investigate the efficiencies at high concentration, the concentration of Zinc is increased at the optimal pressure and PH. Due to the high concentration of Zinc, various concentrations of Zinc are taken into account in the integrated system. As previously mentioned, in order to evaluate the performance of the integrated absorption column and the RO membrane system at a higher concentration of Zinc, wastewater with different concentrations enter the system and the efficiency of each parameter is measured. The results are summarized in Table 6. As can be seen in table 6, increasing the initial Zn concentration from 30 mg/l to 70 mg/l decreases the TDS and EC up to 3%, which denotes that the interaction between various ions in RO Membrane is interrupted by Zn which is compatible with previous studies (Al-Rashdi, Johnson et al. 2013); (Mirbagheri, Biglarijoo et al. 2016). Moreover, this decrease may be due to the blockage of the pores and cake layers formed on the surface membrane (Almojjly, Johnson et al. 2019). However, this is not true for Zn removal, with the removal efficiencies decreasing from 100% to 97.5%, and increasing from 97.5% to 98% afterward and thus, the concentration of 30 mg/l with the removal efficiency of 100% is considered to be optimal. Moreover, it can be seen that the removal efficiencies of Zn change linearly at a high concentration because the flux dependence on concentration is not significant at high concentration which is compatible with the previous study (Bakalár, Búgel et al. 2009). It is worth mentioning that by increasing the concentration of Zn, the efficiencies of all parameters are almost above 90% due to a high rejection of the RO which is desirable (Gu, Kang et al. 2019) ;(Ahmadizadeh, Shokrollahzadeh et al. 2020) and denotes that at higher concentration, the integrated system has an excellent performance.

**Table 6.** Effect of Higher Concentrations of Zn on removal efficiencies at optimum pH and optimum pressure

| $C_{Zn}$ (mg/lit) | Tu (NTU) | $C_{Zn}$ (mg/lit) | TDS (mg/lit) | EC (μmohs/cm) |
|---|---|---|---|---|
| 30 | 95.3 | 100 | 98.1 | 97.4 |
| 50 | 92.4 | 97.5 | 94.3 | 94.5 |
| 70 | 86.3 | 98 | 92.9 | 93.7 |

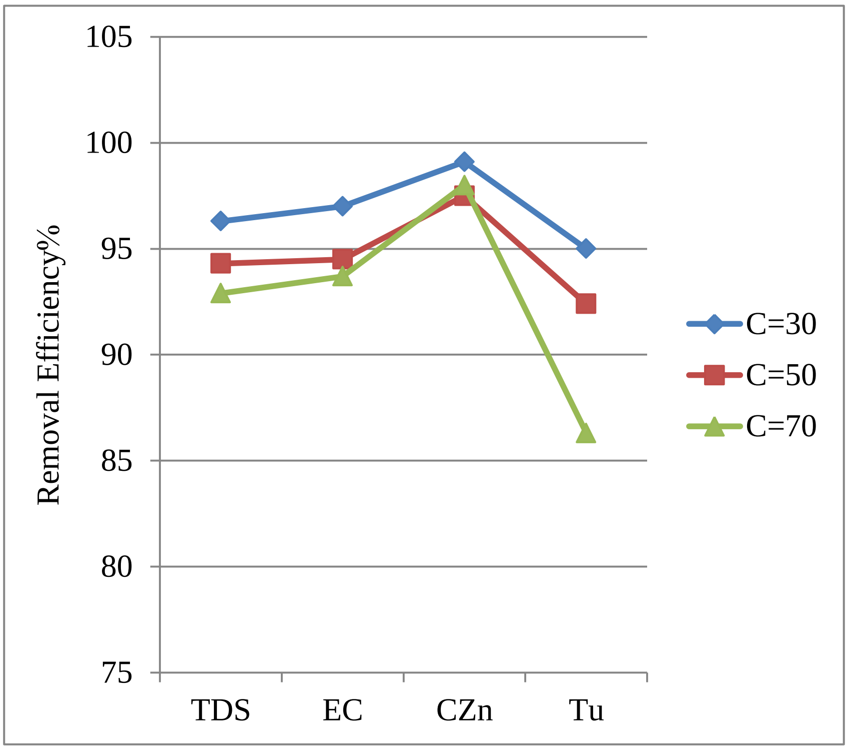


**Fig. 5.** Effect of High concentrations of Zn on removal efficiencies at optimum pH and pressure

## 4- Conclusion

In recent years, the issue of water conservation, wastewater and water treatment has become noteworthy. The steel industry is one of the most widely used water industries, which includes several heavy metals in its wastewater. For the treatment of industrial wastewater, the adsorption column method and membrane filtration can be utilized instead of using chemicals such as: coagulation, flocculation, disinfection. The main goal of this study is to introduce an integrated system of RO adsorption column and membrane filtration which can remove the heavy metal Zinc and reduce TDS and EC. The parameters studied are pH (4.5, 6.5, 7 and 9), pressure (5, 7, 9 and 11 bar) and Zinc concentration (30, 50, 70 mg/l), which are investigated at constant temperature and flow rate. Based on the obtained results, the following conclusions could be drawn:

- The applied pressure does not have a high influence on the removal efficiencies of Zn. By increasing the pressure of heavy metal Zinc from 5 to 9 bar, the removal efficiency would remain the same. This may be due to the deterioration of organic materials and the enrichment of non-biodegradable membrane-rejected substances in the raw water. The optimal pressure achieved is 9 bar at which the highest Zn removal occurs.
- As the pH value increases, the removal efficiency increases. This may be because of the change in pore size and nature of the membrane surface charge which may affect the membrane separation by hydration on the membrane and the absorption capacity of the solutes. Although the removal efficiency at pH of 9 reaches the high of 100%, due to the destruction of Nano adsorbent's surface at high pH values, the optimal pH is considered to be 7.5.
- By increasing the initial Zn concentration from 30 mg/l to 70 mg/l, the removal efficiencies of the TDS and EC are decreased by 3% due to the pore blockage, which shows that Zn interrupts the interaction between various ions in the RO membrane. While, the removal efficiencies of Zn removal are decreased by 2.5%, followed by a 0.5% increase. This marginal change in removal efficiency maybe because the flux dependence on concentration is not significant at high concentration. Therefore, the concentration of 30 mg/l with the removal efficiency of 100% is considered to be optimal. Moreover, by increasing the concentration of Zn, the efficiencies of all parameters are almost above 90% due to a high rejection of the RO, which can be desirable; this denotes that the integrated system also performs well at a higher concentration.

## Credit authorship contribution statement

**Azadeh Kalateh Arabi:** Conceptualization, Writing-Original Draft, Formal Analysis. **Babak Akram:** Writing, Reviewing, Editing. **Seyed Ahmad Mirbagheri:** Supervision, Project Administration**. Ghazaleh Yousofizinsaz:** Writing.

## Declaration of Competing Interest

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

## 5- References


Ahmadizadeh, R., et al. (2020). "Application of halophilic microorganisms in osmotic membrane bioreactor (OMBR) for reduction of volume and organic load of produced water." Journal of Water Process Engineering 37: 101422.

Al-Jlil, S. A. and O. A. Alharbi (2010). "Comparative study on the use of reverse osmosis and adsorption process for heavy metals removal from wastewater in Saudi Arabia." Research Journal of Environmental Sciences 4(4): 400-406.

Al-Rashdi, B., et al. (2013). "Removal of heavy metal ions by nanofiltration." Desalination 315: 2-17.

Almojjly, A., et al. (2019). "Optimisation of the removal of oil in water emulsion by using ceramic microfiltration membrane and hybrid coagulation/sand filter-MF." Journal of Water Process Engineering 27: 15-23.

Arias-Navarro, M., et al. (2019). "The use of respirometry as a tool for the diagnosis of wastewater treatment plants. A real case study in Southern Spain." Journal of Water Process Engineering 29: 100791.

Arora, M., et al. (2004). "Use of membrane technology for potable water production." Desalination 170(2): 105-112.

Babel, S. and T. A. Kurniawan (2003). "Low-cost adsorbents for heavy metals uptake from contaminated water: a review." Journal of hazardous materials 97(1-3): 219-243.

Bakalár, T., et al. (2009). "Heavy metal removal using reverse osmosis." Acta Montanistica Slovaca 14(3): 250.

Beh, C., et al. (2012). "Removal of heavy metals from steel making wastewater by using electric arc furnace slag." Journal of Chemistry 9(4): 2557-2564.

Brahmi, K., et al. (2018). "Treatment of heavy metal polluted industrial wastewater by a new water treatment process: ballasted electroflocculation." Journal of hazardous materials 344: 968-980.

Chaturvedi, S. and P. N. Dave (2012). "Removal of iron for safe drinking water." Desalination 303: 1-11.

Chaudhury, S., et al. (2019). "Highly selective separation of pertechnetate from wastewater." Journal of Water Process Engineering 31: 100896.

Crini, G. (2005). "Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment." Progress in polymer science 30(1): 38-70.

Crini, G. and E. Lichtfouse (2019). "Advantages and disadvantages of techniques used for wastewater treatment." Environmental Chemistry Letters 17(1): 145-155.

Crini, G., et al. (2019). "Conventional and non-conventional adsorbents for wastewater treatment." Environmental Chemistry Letters 17(1): 195-213.

Gu, S., et al. (2019). "Clay mineral adsorbents for heavy metal removal from wastewater: a review." Environmental Chemistry Letters 17(2): 629-654.

Haydar, S., Anis, M., & Afaq, M. (2020). Performance evaluation of hybrid constructed wetlands for the treatment of municipal wastewater in developing countries. Chinese Journal of Chemical Engineering, 28(6), 1717-1724.

Huang, X.-F., et al. (2011). "Advanced treatment of wastewater from an iron and steel enterprise by a constructed wetland/ultrafiltration/reverse osmosis process." Desalination 269(1-3): 41-49.

Kong, X., et al. (2020). "Management of concentrate and waste streams for membrane-based algal separation in water treatment: A review." Water Research: 115969.

Kumari, P., et al. (2019). "Usage of nanoparticles as adsorbents for wastewater treatment: An emerging trend." Sustainable Materials and Technologies 22: e00128.

Li, J., et al. (2020). "Effects of membrane property and hydrostatic pressure on the performance of gravity-driven membrane for shale gas flowback and produced water treatment." Journal of Water Process Engineering 33: 101117.

Mamah, S. C., et al. (2020). "Recent development in modification of polysulfone membrane for water treatment application." Journal of Water Process Engineering: 101835.

Mirbagheri, S. A., et al. (2016). "Removing Fe, Zn and Mn from steel making plant wastewater using RO and NF membranes."

Mohan, D. and C. U. Pittman Jr (2006). "Activated carbons and low cost adsorbents for remediation of tri-and hexavalent chromium from water." Journal of hazardous materials 137(2): 762-811.

Mohan, D., et al. (2011). "Development of magnetic activated carbon from almond shells for trinitrophenol removal from water." Chemical Engineering Journal 172(2-3): 1111-1125.

Murshid, S., & Dhakshinamoorthy, G. P. (2020). Application of an immobilized microbial consortium for the treatment of pharmaceutical wastewater: Batch-wise and Continuous studies. Chinese Journal of Chemical Engineering.

Nataraj, S. K., et al. (2006). "Distillery wastewater treatment by the membrane-based nanofiltration and reverse osmosis processes." Water Research 40(12): 2349-2356.

Nejati, S., et al. (2019). "Biofouling in seawater reverse osmosis (SWRO): Impact of module geometry and mitigation with ultrafiltration." Journal of Water Process Engineering 29: 100782.

Niu, L., Wei, T., Li, Q., Zhang, G., Xian, G., Long, Z., & Ren, Z. (2020). Ce-based catalysts used in advanced oxidation processes for organic wastewater treatment: A review. Journal of Environmental Sciences, 96, 109-116.

Noguchi, M., et al. (2018). "Simultaneous removal and recovery of boron from wastewater by multi-step bipolar membrane electrodialysis." Journal of Water Process Engineering 23: 299-305.

Oubane, M., Khadra, A., Ezzariai, A., El Fels, L., Kouisni, L., & Hafidi, M. (2020). Micronucleus assay based on Vicia faba roots as a tool to assess the performances of wastewater treatment systems. Environmental Technology & Innovation, *19*, 100903.

Shinde, P. A., et al. (2020). "An integrated approach of adsorption and membrane separation for treatment of sewage water and resource recovery." Journal of Water Process Engineering: 101795.

Sirajuddin, A., et al. (2010). Wastewater treatment technologies commonly practiced in major steel industries of India. 16th annual international sustainable development research conference.

Stafiej, A. and K. Pyrzynska (2007). "Adsorption of heavy metal ions with carbon nanotubes." Separation and purification technology 58(1): 49-52.

Svetozarević, M., Šekuljica, N., Knežević-Jugović, Z., & Mijin, D. (2021). Agricultural waste as a source of peroxidase for wastewater treatment: Insight in kinetics and process parameters optimization for anthraquinone dye removal. Environmental Technology & Innovation, *21*, 101289.

Tan, H.-F., et al. (2020). "Future perspectives of nanocellulose-based membrane for water treatment." Journal of Water Process Engineering 37: 101502.

Tang, M., Li, F., Yang, M., & Zhang, Y. (2020). Degradation of kanamycin from production wastewater with high-concentration organic matrices by hydrothermal treatment. Journal of Environmental Sciences, 97, 11-18.

Tchobanoglous, G., et al. (2003). Eddy, Inc, McGraw-Hill: Boston: 1-10.

Wadhawan, S., et al. (2020). "Role of nanomaterials as adsorbents in heavy metal ion removal from wastewater: A review." Journal of Water Process Engineering 33: 101038.

Wuana, R. A. and F. E. Okieimen (2011). "Heavy Metals in Contaminated Soils: A Review of Sources, Chemistry, Risks and Best Available Strategies for Remediation." ISRN Ecology 2011: 402647.

Zagklis, D. P., et al. (2015). "Purification of olive mill wastewater phenols through membrane filtration and resin adsorption/desorption." Journal of hazardous materials 285: 69-76.

Zheng, X., et al. (2015). "Overview of membrane technology applications for industrial wastewater treatment in China to increase water supply." Resources, Conservation and Recycling 105: 1-10.