Environmental Protection Research
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Research Article

Treatment and Desalination of Wastewater Generated After Steel Degreasing and Pickling in the Tunisian Galvanization Industry

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Received: 21 November 2023; **Revised:** 12 March 2024; **Accepted:** 22 March 2024

Abstract: A case study of galvanization wastewater treatment was carried out to preserve the environment and to suggest a solution to the Metal Galvanization of Poulina Group Holding MBG-Galva industry located in Tunisia for reducing effluent organic matter, heavy metals, and salt contents. The current industry had two baths of rinsing water after steel degreasing and pickling steps. The chemical oxygen demand (COD) and pH of the first bath were very high compared to the second bath, which exhibits a low pH with high salinity and high heavy metals contents. Coagulation-flocculation and electrodialysis were examined as treatment processes for rinse water obtained after steel degreasing, while precipitation-oxidation and membrane distillation were combined for pickling rinse water treatment. Aluminum sulfate and sodium alginate were used, respectively, as coagulants and flocculents under optimal conditions determined through the Jar test. After the electrodialysis step, the removal rates were found to be 89.6% for conductivity, 93% for COD, 90 to 96% for salt content, and 82% to 99.5% for heavy metals. For the second effluent, the conductivity of wastewater was reduced by 97%, and heavy metals and COD were removed. The lab-scale experiment implementation proved that using the current process has a high impact on obtaining zero liquid reject in the manufactory, and reusing it in the same bath is an opportunity for water preservation. Solid waste characterized by X-rays showed that lead oxide and iron can be recovered from galvanization industry wastewater. Scaling the combined pretreatment and desalination system in a demonstration unit helps the galvanization industry reuse the water in the same industry and prevent environmental pollution.

Keywords: galvanizing process, electrodialysis, coagulation, flocculation, membrane distillation, heavy metals

1. Introduction

The galvanizing industry generated wastewater rich in toxic compounds that hurt the environment [1]. It helps to protect steel from corrosion with zinc addition [2], but it consumes a high amount of water and acid that can be treated and reused in the same process. To treat the galvanization wastewater, several types of treatments were published in the literature: ion exchange [3], coagulation-flocculation [2], combined photocatalytic oxidation and coagulation [4], adsorption on magnetic nanoparticles [5], and oxidation-electrolysis and precipitation [6]. The main objective of the published papers focused on galvanization wastewater treatment, which was to remove heavy metals. However, the salinity, turbidity, and chemical oxygen demand (COD) were also high due to grease and concentrated hydrochloric acid (HCl) addition in steel treatment steps. More precautions should be adopted to reduce the amount of tap water

DOI: https://doi.org/10.37256/epr.4120243976

used in the surface treatment and galvanization industries and more sophisticated processes need to be used to remove harmful compounds and protect the environment. MBG-Galva industry discharged a substantial volume of rinse water, consisting of two baths from steel degreasing and six baths from steel pickling with HCl (32%), directly into the sewer. The coagulation-flocculation and electrodialysis were tested for the first case, and precipitation using sodium hydroxide combined with the oxidation process and membrane distillation were tested to treat the second-generated wastewater.

2. Materials and methods

2.1 *Case study*

The MBG-Galva manufactory, located in the north of Tunisia in the Nabeul Government, is one of the most important industries in Tunisia. It was a part of the Poulina Holding Group, and one of its activities was the hot dip galvanizing of steel. Different steps were taken before adding zinc to steel. After hanging, the metal piece (Figure 1) was immersed in a bath of sodium hydroxide and emulsifiers to remove grease, and then the metal piece was rinsed in another bath of water (Figure 1). After degreasing and rinsing, the piece was pickled in six successive baths of HCl (32%), followed by a rinsing step in water. Before the metal coating, the steel was fluxing and drying. Every 15 days, the rinse water of the steel after degreasing and pickling was changed by tap water. The wastewater generated from this industry had very bad quality, and it was sent directly to the sewer after dilution.

(A)

(B)

Figure 1. Photo of MBG-Galva steel galvanization steps; (A) hanging, (B) steel degreasing, pickling, and water rinse

2.2 *Samples and wastewater characterization*

Samples of wastewater were taken from the two steps of steel rinsing in the MBG-Galva industry in different periods and then transferred to the Water Research and Technologies Center for analysis and treatment. A sensION+ conductimeter, a Proline pH meter, and a Turb 555 were used for conductivity, pH, and turbidity measurement, respectively. The MA. 315 - COD method is used for COD measurement [7]. The Total Kjeldhal Nitrogen (TKN), ammonia nitrate, and sulfate are analyzed according to the method published by Rodier et al. [8]. The heavy metals (cadmium, lead, total chromium, iron, and manganese), and ion contents (calcium, magnesium, and aluminum) were characterized using atomic absorption spectroscopy (AAS Vario 6), sodium and potassium were measured using a flame emission spectrophotometer (ELICO), and chloride was analyzed by the conductivity evolution method due to the range of pH.

2.3 *Treatment of wastewater generated after steel degreasing and rinsing*

To reduce the COD, the coagulation-flocculation process was used in this study, and then electrodialysis was applied to decrease wastewater salinity and heavy metals (Figure 2).

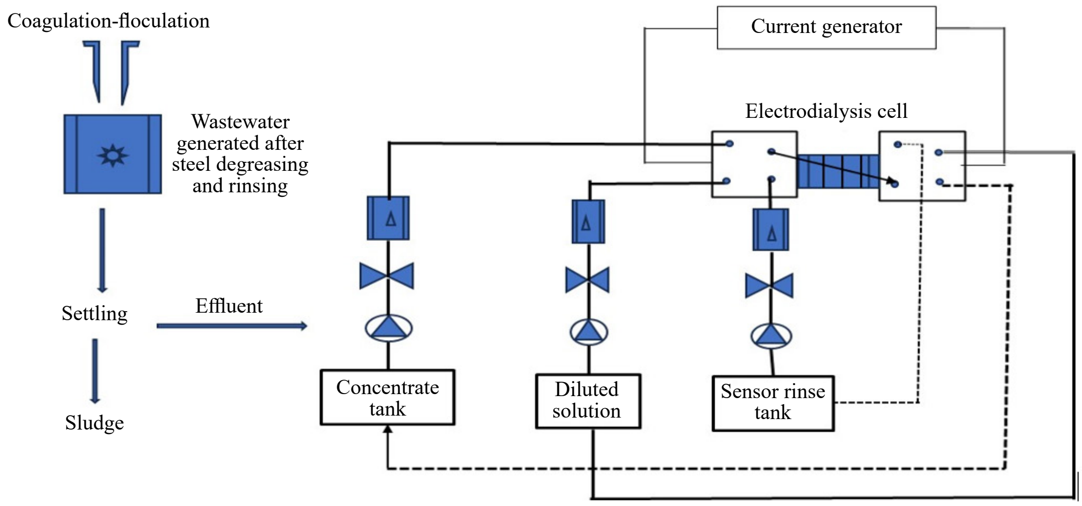

Figure 2. Treatment of wastewater generated after steel degreasing and rinsing

2.3.1 *Optimization of coagulation-flocculation process*

The coagulant used in this work was aluminum sulfate ($Al_2 (SO_4)_3.18H_2O$) and the flocculent was the alginate sodium. The optimization of parameters was carried out through a Jar test where the pH, coagulant concentration, and flocculent concentration were systematically adjusted within the ranges of 13 to 4, 0.3 to 1.2 g/L, and 0.05 to 1 g/L, respectively. Throughout the experiment, the coagulation stirrer velocity remained constant at 150 rpm for 15 minutes, while the flocculation stirrer velocity was set at 40 rpm for 10 minutes.

2.3.2 *Electrodialysis unit description*

The electrodialysis desalination unit (Figure 2) was performed on a laboratory scale. A PC cell, ED 64-004 (made in Germany), was used, and it was made of two polypropylene blocks supporting electrodes. Two sensors are used: Pt/Ir-coated Ti stretched as the anode and Ti stretched metal as the cathode. Seven anion-0.5 mm flow spacers and cationic Neosepta membranes are introduced between the two sensors. Three pumps are used for recirculated dilute, concentrated waters, and the sensors rinsing solution. The flow rates were measured using flowmeters, and the rinse sensor solution of Na_2SO_4 (0.1 M) was used to avoid hypochlorite generation.

2.4 *Treatment of wastewater generated after steel pickling and rinsing*

As illustrated in Figure 3, precipitation using sodium hydroxide and oxidation processes was combined with membrane distillation to treat wastewater generated after steel pickling and rinsing. 1.5 mg/L of anionic flocculent was added to improve sedimentation. The used membrane was polyvinylidene fluoride, with a pore size of 0.45 μm, a thermal conductivity of 0.041 $Wm^{-1}K^{-1}$, and an active area of 3.2 x 10^{-3} m^2.

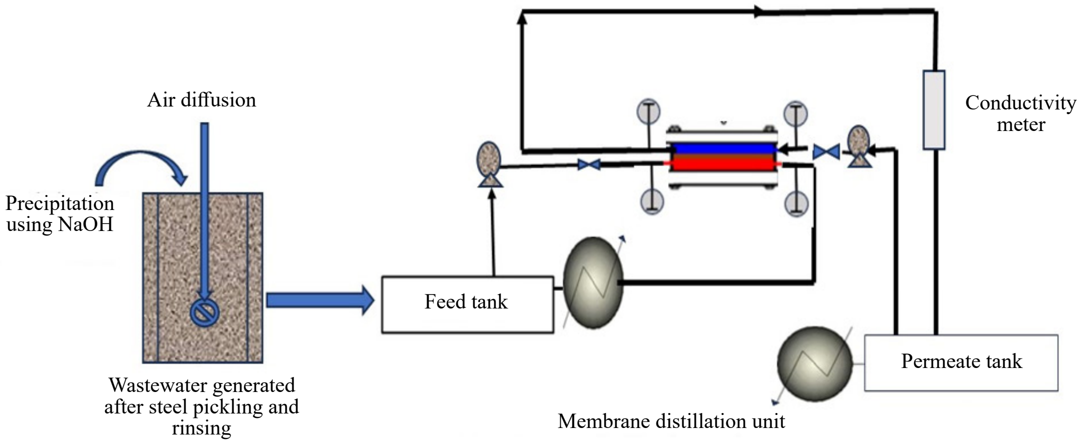

Figure 3. Treatment of wastewater generated after steel pickling and rinsing

2.5 *Sludge analysis*

The residual sludge generated by wastewater treatment after coagulation-flocculation and precipitation-oxidation was analyzed by X-ray type D8 Advance BRUKE.

3. Results and discussions

3.1 *Rinse water treatment after steel degreasing*

3.1.1 *Optimum conditions of coagulation-flocculation process*

The initial wastewater after steel degreasing and rinsing had a pH of 13, a conductivity of 12.5 mS/cm, and a turbidity of 375 NTU (Nephelometric Turbidity unit).

As shown in Figures 4, 5, and 6, after the Jar test, the pH of 5 and the coagulant concentration of 0.9 g/L were the optimum conditions. The turbidity and the conductivity were reduced by 97% and 16%, respectively. The flocculent concentration of 0.25 g/L improved the removal rate of conductivity (24%). Compared to the literature, Arroub and Elharfi [9] used a concentration of coagulant and flocculent less than used in this work to treat effluent from Galvacier's various hot-dip galvanizations: 0.2 g/L lime as a coagulant and 0.2 g/L chitosan as a flocculent. They obtained removal rates of 97% and 97.9% for turbidity and conductivity, respectively. Hazourli et al. [10] used the same coagulant as the current research work to treat wastewater generated after painted steel tiles, and they obtained the same optimum pH (5), a coagulant concentration of 0.7 g/L, and 1 ppm for cationic flocculent (SP6). They obtained, using these conditions, a removal rate of 99.3% of wastewater turbidity, which was 800 NTU before treatment.

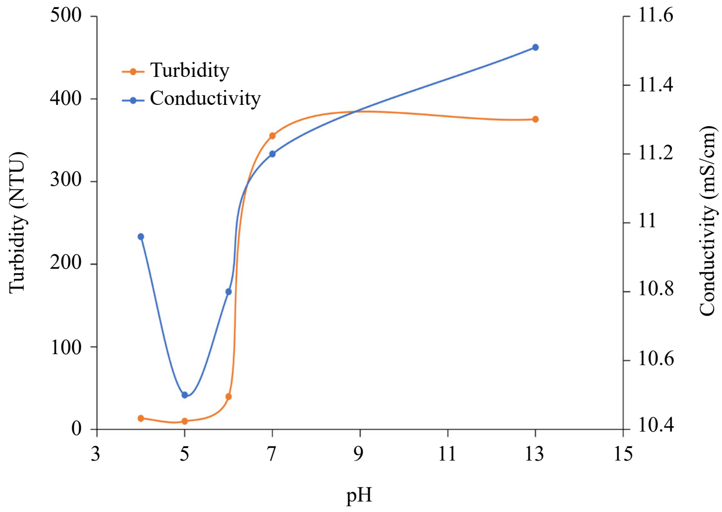

Figure 4. Jar test result after pH variation

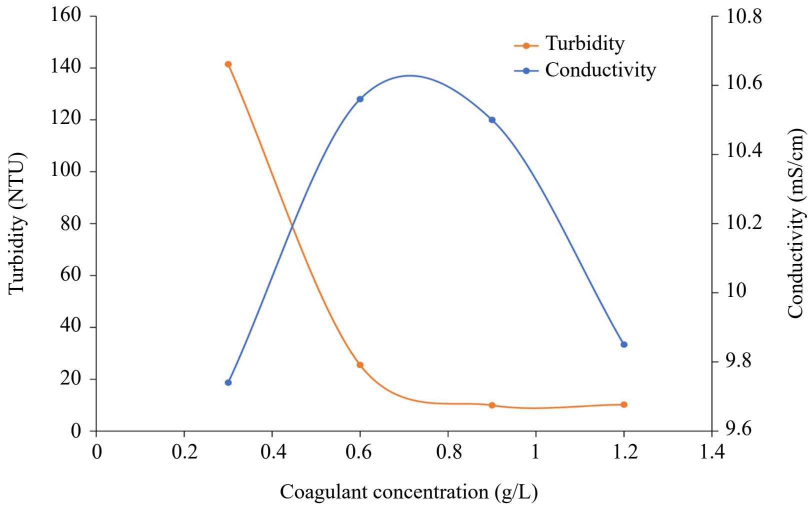

Figure 5. Jar test result after coagulant concentration variation

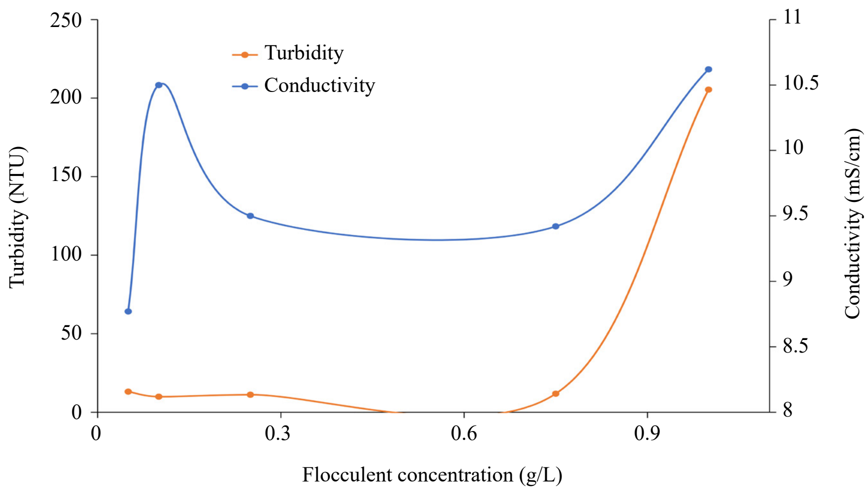

Figure 6. Jar test result after flocculent concentration variation

3.1.2 *Desalination of effluent by electrodialysis*

The treatment of the effluent from the coagulation-flocculation process applied to steel rinse water after degreasing through electrodialysis (Figure 7) resulted in a notable reduction in water conductivity by 89.6%. Electrodialysis demonstrated efficiency in reducing salt content, heavy metals, and organic pollution. Specifically, electrodialysis achieved the removal of 96% of chloride, 90% of sulfate, and 92% of sodium and potassium. As indicated in Table 1, before treatment, the effluent COD, chloride, sulfate, and sodium contents were more than 2 g/L for each. The lead affluent content was 80 times higher and the iron content was 60 times higher than the standard values. After treatment using hybrid processes (coagulation-flocculation and electrodialysis), high removal rates were observed for heavy metals, with complete removal for cadmium and manganese, 99.58% for lead, 97% for zinc and iron, 89% for copper, and 82% for total chromium. Moreover, electrodialysis successfully removed 93% of COD through the same technique.

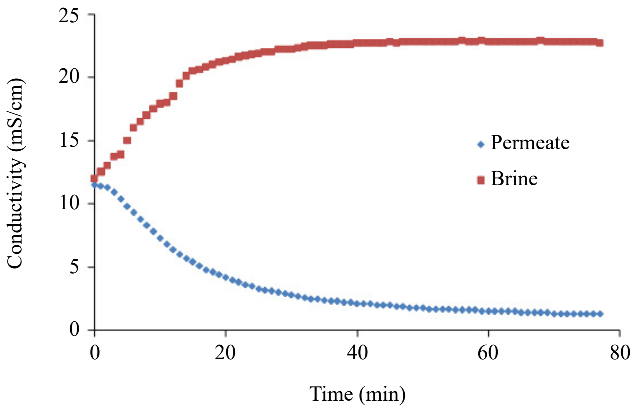

Figure 7. Evolution of concentrate and permeate conductivities during the treatment of wastewater by electrodialysis at 10 volts

Table 1. Analysis of rinsing water after steel degreasing before and after treatment with coagulation-flocculation combined with electrodialysis

Parameters	Unit	Raw water	Treated water	Tunisian standard 106.02
pH		13	3.49	6.5 < pH < 8.5
Conductivity T = 20.1 °C	mS/cm	12.5	1.3	5
COD	mg O_2/L	3473.3	228	1,000
Chloride	mg/L	4544	170	700
Sulfate	mg/L	3662.01	353.46	400
Potassium	mg/L	16.7	1.2	-
Sodium	mg/L	2360	170	-
Aluminum	mg/L	2.13	0.1	10
Nitrate	mg/L	482.84	15.47	90
Orthophosphate	mg/L	64	25.55	10
Iron	mg/L	278.5	5.68	5
Copper	mg/L	0.93	0.1	1
Manganese	mg/L	29	0	1
Zinc	mg/L	27	0.7765	5
Cadmium	mg/L	0.197	0	0.1
Total chromium	mg/L	1.8	0.31	2
Lead	mg/L	80	0.33	1

Furthermore, it is noteworthy that all the parameters met the restrictions outlined in the Tunisian standards, allowing the treated effluent to be safely discharged into the sewer system. Electrodialysis was applied for the first time to treat effluent from the galvanization industry, and good results were obtained. Generally, this technique is used to purify the acid used in the pickling process and reuse it in the same bath. Purifying the water and reusing it to rinse the metal was also an alternative to preserve water in countries such as Tunisia, which suffers from water scarcity, and to protect the environment by removing heavy metals and salts that hurt bacteria growth in the wastewater treatment plant if this effluent was sent directly to the sewer.

The specific consumed energy deduced from the evolution of intensity during the time was 6 KWh/m^3, which is higher compared to reverse osmosis and nanofiltration (Figure 8). Using a photovoltaic panel can preserve energy in this case, which is higher than when reverse osmosis specifically consumes energy.

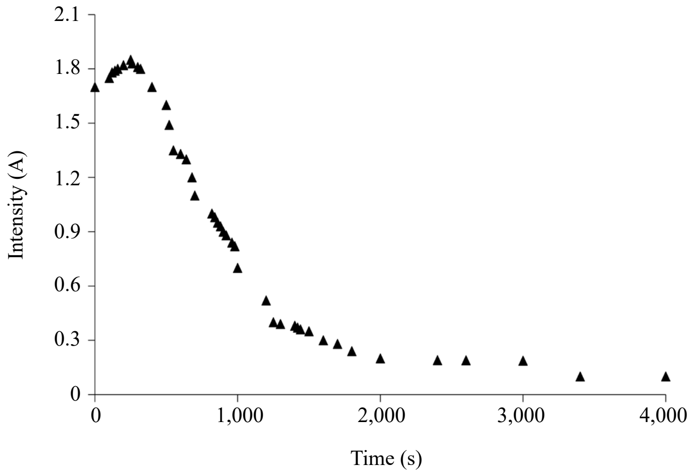

Figure 8. Evolution of the intensity during the treatment of wastewater by electrodialysis at 10 volts

Makisha and Yunchina [11] compared chemical processes and membrane processes for galvanization wastewater treatment, and they observed that the best quality can be obtained by reverse osmosis, which can help to recover 60% of good water quality and reuse it in the same industry. However, expensive pretreatment steps should be implemented to avoid membrane fouling by grease and suspended solids. Electrodialysis was rarely applied for this type of effluent. Benalla et al. [12] used electrodialysis to treat the rinsing wastewater generated in surface treatment brassware and showed that around 95-98% of heavy metals were removed by this technique.

3.2 *Rinse wastewater treatment after steel pickling*

The untreated wastewater following steel pickling and rinsing exhibited a very high conductivity (68.4 mS/cm) with higher heavy metal content, including 8.3 g/L of iron and 0.4 g/L of zinc. The chloride content was notably high at 15.96 g/L, attributed to the concentrated HCl used in the steel pickling process (Table 2). Discharging this effluent directly into the sewer poses considerable harm due to its detrimental composition.

3.2.1 *Efficiency of precipitation-oxidation process in rinse wastewater treatment after steel pickling*

The precipitation using sodium hydroxide and oxidation treatment applied to the rinse water after steel pickling resulted in a substantial decrease in effluent conductivity by 62.7%. This reduction can be attributed to the precipitation of heavy metals at elevated pH levels and the oxidation of iron to iron oxide. Notably, the treatment exhibited impressive removal rates for heavy metals, achieving 99.9% for iron, 94.3% for copper, 99.7% for manganese, 99.4% for zinc, 27.3% for cadmium, 88.5% for total chromium, and 74.7% for lead (Table 2). The lime was also tested in this work but generated a high amount of sludge and a small amount of water with an efficiency less than sodium hydroxide.

Table 2. Analysis of rinsing water after metal pickling before and after treatment

Parameters	Unit	Sample before treatment	Sample after precipitation-oxidation	Sample after pretreatment and membrane distillation	Tunisian standard 106.02
pH		1.5		5.98	$6.5 < pH < 8.5$
Conductivity T = 20.1 °C	mS/cm	68.4	25.5	2	5
COD	mg O_2/L	1839.54	-	-	1,000
Chloride	mg/L	15,975	15,000		700
Iron	mg/L	8,376	0.66	0	5
Copper	mg/L	3.86	0.22	0	1
Manganese	mg/L	32	0.07	0	1
Zinc	mg/L	483	2.5	0	5
Cadmium	mg/L	0.23	0.17	0	0.1
Total chromium	mg/L	3.23	0.37	0	2
Lead	mg/L	5.85	1.48	0	1

As illustrated in Figure 9, a significant quantity of sludge, enriched with iron oxide and heavy metals, is effectively removed through the treatment process. This results in a substantial improvement in the overall quality of the water. The achieved results demonstrated that the elevation of pH and aeration can help the industry remove iron from wastewater and reuse it in the same baths for steel rinsing after pickling.

Figure 9. Sludge obtained after precipitation and oxidation of rinse water after steel pickling

The sludge generated by the treatment process was analyzed by X-ray (Figure 10), and according to the pictures (31.773°, 45.522°, 56.468°, 75.309°, and 83.969°), sludge contains Fe_2Si and PbO, which can be recovered.

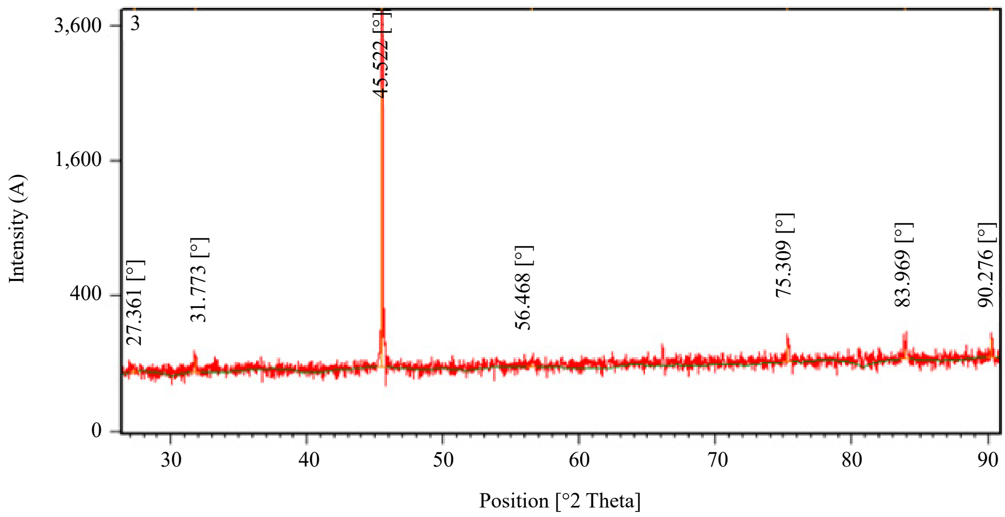

Figure 10. X-ray analysis of solid sludge

Discharging the sludge in the trash dump damages the soil with heavy metal infiltration, such as lead and iron. The best alternative was to recover the heavy metal oxide and purify it.

3.2.2 *Efficiency of membrane distillation in rinse wastewater treatment after steel pickling and precipitation-oxidation*

Membrane distillation was a sophisticated process rarely used in Tunisia in real-scale wastewater treatment. In this work, we try to use it to prevent the fouling of reverse osmosis by iron oxide. As depicted in Figure 11, the orange color attributed to iron is effectively eliminated through membrane distillation. The combined treatment of membrane distillation with oxidation-precipitation, as outlined in Table 2, led to a significant reduction in conductivity from 68.4 to 2 mS/cm, accompanied by a substantial decrease in iron content from 8 g/L to 0 g/L. These proposed solutions demonstrate a significant positive impact, enabling the treated wastewater to be reused within the same manufacturing facility, thereby conserving water resources and safeguarding the environment. Notably, the achieved results surpass the heavy metal removal rates reported in various techniques outlined in the literature (Table 3). The salinity of effluent can be attributed to the generation of Cl_2 after the evaporation of water rich in HCl and to its recovery after condensation in an aqueous solution.

Figure 11. Membrane distillation treatment of rinse wastewater after steel pickling and treatment by precipitation-oxidation

Table 3. Overview of different techniques and their efficiency used in literature to treat rinse wastewater after steel pickling

Techniques	Results	References
Ion exchange	% of metal eluted	
Amberlite IR 120	85% of zinc and 100% of iron	[3]
Lewatit SP 112	62% of zinc and 66% of iron	
Magnetic nanoparticles adsorption (Fe_3O_4)	Treatment of wastewater of Ghatasha Galvanization Company, El Fawwar Palestine The removal rate of zinc was more than 95%	[5]
Limestone (particle size 5 mm) packed aerated bed filter (0.5 h) + batch neutralization reactor (residence time 1 h) +	The removal rate of iron was 99.8%	[13]
Membrane filtration (polytetrafluoroethylene, flux 0.4 m3/m2.h, diameter 2.5 m, and porosity 0.2 µm)	Influent 1.5 g/L Effluent 2 mg/L	
Neutralization using CaO waste from pulp and paper industries (52 g/L)	pH increases from 1.3-2.4 to 9 Efficient removal of chromium (99.98%,), iron (99.99%), nickel (99.99%), zinc (99.33%), and molybdate (95.67%)	[14]
Membrane distillation Polytétrafluoroéthylène membrane, pore size 0.45 µm	Removal of more than 99.99% of iron	[15]
Ultrafiltration (UP150, 4 bar, 400 L/h, area 6 m^2) +	Treatment of rinse wastewater after pickling (Influent Conductivity 35.9 mS/cm, pH 4.1, zinc 2.5 g/L, and chloride 11.04 g/L)	[16]
Reverse osmosis (TM710, 30 bar, 150 L/h, area 8.1 m^2)	The removal rate of chloride and zinc was 99%	
Biosorption	Adsorption of 8.64 mg/g of metals	
Eclipta alba Calcinated egg shells	Removal rate of heavy metals higher than 95% 100% removal of iron More than 90% removal rate of chromium	[17]

4. Conclusion

The effectiveness of two treatment processes was tested for galvanizing rinsing water. The first was the hybrid coagulation-flocculation and electrodialysis treatment processes applied for rinsing water after steel degreasing. Using this hybrid system, 97%, 89.6%, and 93% removal rates were obtained for turbidity, conductivity, and COD, respectively. For heavy metals, 100% of cadmium and manganese, 99.5% of lead, 97% of zinc and iron, 89% of copper, and 82% of total chromium were also removed. The second hybrid system was oxidation combined with membrane distillation after steel pickling in concentrated HCl. Treated wastewater from the two-rinsing baths was highly improved, and it can be reintroduced in the same baths for metal washing purposes. The perspective of this work is to use nanocomposite membranes to treat galvanizing industry wastewater and recover the metal from concentrated HCl.

Conflict of interest

There is no conflict of interest for this study.

References

[1] Fresner J, Schnitzer H, Gwehenberger G, Planasch M, Brunner C, Taferner K, et al. Practical experiences with the

implementation of the concept of zero emissions in the surface treatment industry in Austria. *Journal of Cleaner Production*. 2007; 15(13-14): 1228-1239. https://doi.org/10.1016/j.jclepro.2006.07.024
[2] Berradi M, Chabab Z, Arroub H, Nounah H, El Harfi A. Optimization of the coagulation/flocculation process for the treatment of industrial wastewater from the hot dip galvanizing of steel. *Journal of Materials and Environment Science*. 2014; 5(2): 360-365.
[3] Marañón E, Fernández Y, Castrillón L. Ion exchange treatment of rinse water generated in the galvanizing process. *Water Environment Research*. 2005; 77(7): 3054-3058. https://doi.org/10.2175/106143005X73947
[4] Abdel Wahaab R, Moawad AK, Taleb EA, Ibrahim HS, El-Nazer HAH. Combined photocatalytic oxidation and chemical coagulation for cyanide and heavy metals removal from electroplating wastewater. *World Applied Sciences Journal*. 2010; 8(4): 462-469.
[5] Sawalha H, Al-Jabari M, Tamimi I, Shahin M, Tamimi Z. Characterization and treatment of wastewater from galvanization industry in Palestine. *International Journal of Environment & Water.* 2016; 5(3): 37-44.
[6] Zhen-Gong T. Treating the galvanization wastewater by a complex process. *BioTechnology: An Indian Journal.* 2013; 8(8): 1108-1112.
[7] Centre d'expertise en analyse environnementale du Québec. *Détermination de la demande chimique en oxygène : méthode de reflux en système fermé suivi d'un dosage par colorimétrie avec le bichromate de potassium. MA. 315 – DCO 1.1 (révision 7)*. Québec, Canada: Ministère de l'Environnement du Québec; 2023. https://www.ceaeq.gouv.qc.ca/methodes/pdf/methode-analyse-315-demande-chimique-oxygene.pdf
[8] Rodier J, Legube B, Merlet N, Brunet R. *L'analyse de l'eau: Eaux naturelles, eaux résiduaires, eau de mer.* 9th ed. Paris: Dunod; 2009.
[9] Arroub H, Elharfi A. Comparison of the effectiveness of new couples in the treatment of effluents from hot-dip galvanizing. *International Journal of ChemTech Research*. 2018; 11(3): 334-341. http://dx.doi.org/10.20902/IJCTR.2018.110345
[10] Hazourli S, Ziati M, Benredjem Z, Delimi R, Boudiba L. Analysis of wastewater loaded with paint before and after treatment of coagulation-flocculation. *Arabian Journal of Science and Engineering*. 2012; 37: 897-903. https://doi.org/10.1007/s13369-012-0219-0
[11] Makisha N, Yunchina M. Methods and solutions for galvanic wastewater treatment. *MATEC Web of Conferences.* 2017; 106: 07016. https://doi.org/10.1051/matecconf/201710607016
[12] Benalla S, Bachiri B, Touir J, Tahaikt M, Taky M, Touhami ME, et al. Feasibility of electrodialysis in heavy metals removal from brassware wastewaters. *Desalination and Water Treatment*. 2021; 240: 106-114. https://doi.org/10.5004/dwt.2021.27721
[13] Zhang J, Chen G, Ma Y, Xu M, Qin S, Liu X, et al. Purification of pickling wastewater from the steel industry using membrane filters: Performance and membrane fouling. *Environmental Engineering Research*. 2022; 27(1): 200486. https://doi.org/10.4491/eer.2020.486
[14] Jarnerud T, Karasev AV, Jönsson PG. Neutralization of acidic wastewater from a steel plant by using CaO-containing waste materials from pulp and paper. *Materials*. 2021; 14(10): 2653. https://doi.org/10.3390/ma14102653
[15] Cai J, Guo F. Mass transfer during membrane distillation treatment of wastewater from hot-dip galvanization. *Separation and Purification Technology.* 2020; 235: 116164. https://doi.org/10.1016/j.seppur.2019.116164
[16] Kowalik-Klimczak A, Gajewska-Midziałek A, Buczko Z, Łożyńska M, Życki M, Barszcz W, et al. Circular economy approach in the treatment of galvanic wastewater employing membrane processes. *Membranes*. 2023; 13(3): 325. https://doi.org/10.3390/membranes13030325
[17] Charazińska S, Burszta Adamiak E, Lochyński P. The efficiency of removing heavy metal ions from industrial electropolishing wastewater using natural materials. *Scientific Reports*. 2022; 12: 17766. https://doi.org/10.1038/s41598-022-22466-9