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Treatment of Municipal and Industrial Wastewater Effluents Using Integrated Schemes

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Abstract: The motivations for wastewater treatment are numerous due to its environmental and economic merits. An integrated scheme comprising chemical coagulation followed by adsorption was developed for the treatment of different sources of wastewater in order to remove heavy metals and reduce the chemical oxygen demand (COD). Effluents of industrial wastewater rich in Nickel (Ni) and Chromium (Cr) as well as mixed domestic and industrial wastewater from the Egyptian industrial city of Tenth of Ramadan were treated. Chemical treatment was conducted using alum, ferrous sulfate and lime. The optimum dose of coagulant required for the removal of each heavy metal was determined. A consecutive batch adsorption onto Calcium-Bentonite (Ca-B) was undertaken to improve heavy metal removal efficiencies. For the industrial wastewater, Ni was completely removed during the coagulation step using 200 mg/l lime, while 98% of Cr was removed using the integrated scheme with 300 mg/l ferrous sulfate as a coagulant. For the mixed wastewater, chemical treatment reduced COD with an efficiency up to 78% depending on the employed coagulation dose. Furthermore, complete removal of Cr was achieved using all tested coagulants at 100 mg/l, whereas Lead (Pb) was completely removed using alum at 100 mg/l. Complete removal of Ni and Cadmium (Cd) were also achieved using the integrated scheme. Moreover, a pilot-scale tertiary separation system (TriSep) was tested for the treatment of both synthetic and real wastewater samples enriched with Cr and Ni. Almost complete removal efficiencies for both metals was accomplished.

Key words: Adsorption · Calcium-bentonite · Chemical coagulation · Wastewater

INTRODUCTION

Industrial wastewater generally contains high concentration of pollutants such as organic material, heavy metals and toxic compounds. Such wastewater causes environmental and health hazards and, consequently, must be properly treated before final disposal [1]. In Egypt, several waste water treatment plants exceed the allowable limits of biological oxygen demand (BOD) and total suspended solids (TSS) in their effluents (60 mg/l and 50 mg/l, respectively) [2, 3]. Usually 65-90% of the organic matter in wastewater is colloidal or particulate, which can be reduced by chemical pretreatment of raw wastewater. Therefore, chemically enhanced processes can be utilized to improve the efficiency of the primary treatment process and to reduce the cost of the secondary treatment stage [4]. Various wastewater treatment technologies are used including chemical treatment, membrane separation, adsorption, biological treatment and electrochemical treatment. High removal efficiencies of heavy metals and TSS as well as high reduction in BOD and COD were achieved by chemical treatment using ferric chloride, ferric or ferrous sulfate, alum, lime and ionic polymers [5, 6]. Several investigations on the use of clays and zeolites (natural and synthetic) for heavy metal removal have been reported. Pilot tests using kaolinite with sand media filtration removed Zinc (Zn), Copper (Cu) and Lead (Pb) with efficiencies of about 50, 90 and 90%, respectively [7]. Tertiary treatment of municipal wastewater was applied using raw and modified diatomite for the reduction of COD and BOD as well as the removal of nitrates (NO_3), phosphates (PO_4), Arsenic (As), Cd, Pb, Cu and Zn, achieving maximum efficiencies of 72, 82, 70, 78, 54, 90, 90, 95 and 90 %, respectively [8].

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In this paper, the treatment of real wastewaters using chemical and adsorption techniques was conducted to develop an integrated low cost treatment process for the removal of TSS and heavy metals as well as for the reduction of COD. Two sources of real wastewater were tested; a heavy industrial effluent rich in Ni and Cr and a mixed (domestic/industrial) wastewater effluent. The efficiencies of the employed treatment methods were compared to those obtained using the pond oxidation methods currently existing on site. Furthermore, the efficiency of a pilot-scale tertiary separation (Trisep) system for heavy metal removal was tested using synthetic and real wastewater samples enriched with Ni and Cr.

MATERIALS AND METHODS

Materials and Analysis

Wastewater Sources: Three different real industrial wastewater samples were collected. The first sample (EW) was collected from an electroplating facility (Giza, Egypt) and it is characterized by high concentrations of heavy metals mainly Ni and Cr as well as high acidity (pH: 2.9). The two other samples (MW and IW) were collected from Tenth of Ramadan disposal facility (Cairo, Egypt) after on-site mechanical treatment. Sample (MW) comprises municipal wastewater mixed with industrial wastewater while, the other sample (IW) is totally an industrial wastewater. Sample (T1) was prepared by dissolving Ni and Cr salts in water, while sample (T2) was prepared by adjustment of the wastewater sample (IW) through dilution with water and enrichment with Ni and Cr salts such that their concentrations were equal to those present in the synthetic sample (T1).

Heavy Metal Salts, Coagulants and Adsorbents: Analytical grade chemicals from Merck and ADWIC were used in this study. Chromium nitrate and nickel nitrate at different concentrations were used to prepare the synthetic samples. Lime ($Ca(OH)_2$), alum ($Al_2SO_4.18H_2O$) and ferrous sulfate ($FeSO_4.7H_2O$) were used as coagulants. Polyacrylamide (PAM) of 1% (wt) and (MW> 50000 Da) was used as a flocculation aid. Raw calcium-bentonite (Ca-B) of particle size < 106 μm was delivered from International Company of Mining and Investments (Egypt) with a chemical composition depicted in Table 1 [9].

Analysis and Measurements: The concentrations of metal ions were measured using an atomic absorption flame spectrometer (GBC Avanta). Conductivity and PH were measured using HANNA apparatus model-211. Samples were analyzed for COD, BOD and TSS using standard methods [10].

Table 1: Chemical composition of calcium-bentonite [9].

Constituent	%
SiO_2	52.98
TiO_2	1.51
Al_2O_3	20.00
Fe_2O_3	10.02
MgO	1.42
CaO	0.85
Na_2O	1.48
Others	1.54
Loss on ignition	9.94
Moisture content	7.60

Table 2: Trisep technical specifications

Item	Specifications
Filtration unit	Media: graded washed sand, cutoff: = 20μm
Adsorption unit	Resin type: Amberlite IR 120H, exchange capacity: 1.8 q/L (H^+ form) granular activated carbon (AquaSorb 1000, Jacobi carbons), Iodine number: 900 mg/g, methylene blue: 200 mg/g.
RO unit	Membrane module: polyamide thin film composite, BW 30-2540, filmtec, membranes (DOW), surface area 26 m^2, salt rejection 99.5%, max operating pressure 40 bar.

Methods: Wastewater samples, EW and MW, were subjected to an integrated treatment scheme involving chemical coagulation followed by adsorption onto raw Ca-B in order to remove the residual heavy metals. Chemical treatment comprised adjustment of wastewater to neutral pH followed by addition of either alum, lime or ferrous sulfate solutions using varying doses of 100, 200 and 300 mg/l while mixing at 250 rpm for 30 min using jar test apparatus. A flocculation step was also conducted by adding 10 mg/l PAM to some samples with gentle stirring at 70 rpm for 10 minutes followed by settling then filtration. Treatment of wastewater samples (T1 and T2) was investigated on the pilot-scale Trisep system (5m^3/d) which comprises three separation columns of sand, carbon and polymeric resin followed by low pressure Reverse Osmosis (RO) membrane (Fig. 1). Technical specifications of the system are given in Table 2.

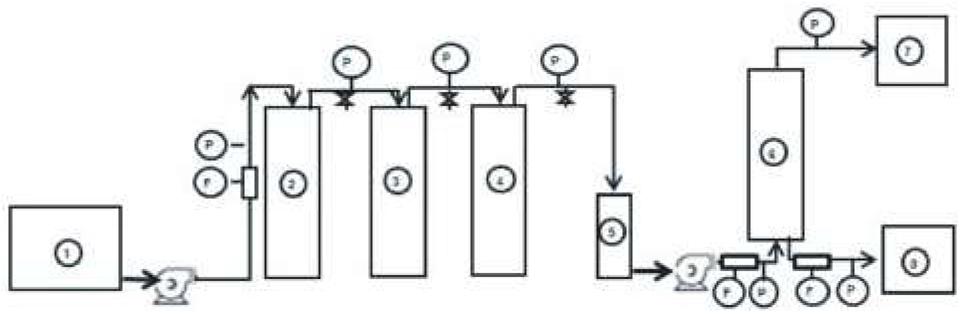


Fig. 1: Schematic diagram for the Trisep setup

1: Waste water feed tank	7: Permeate storage tank
2: Sand filter column	8: Reject storage tank
3: Carboen filter column	F: Flowmeter
4: Ion exchange column	P: Pressure regulator
5: Filter	⋈: Valve
RO membrance system	

RESULTS AND DISCUSSION

Wastewater Characteristics: Characteristics of the investigated wastewater samples (EW and MW) are depicted in Table 3.

Sample (T1) has Ni and Cr concentrations of 2.3 and 1 mg/l, respectively and sample (T2) has concentrations of Ni and Cr same as T1, while COD and TSS are 310 mg/l and 48 mg/l, respectively. It is noted that the original IW sample has a COD and TSS of 850 mg/l and 140 mg/l, respectively and contained Ni and Cr concentrations of 2.25 and 1mg/l, respectively.

Current Wastewater Treatment Plant Performance: The current treatment system at Tenth of Ramadan City comprises primary treatment (mechanical treatment) followed by oxidation ponds. Samples of raw and treated wastewater were collected and analyzed during the interval from August 2011 till April 2012. The treatment system reduced COD from an average value of 1500 mg/l to 700 mg/l and to 200 mg/l. Whereas BOD was reduced from 800 mg/l to approximately 400 mg/l and 150 mg/l, after mechanical and pond treatment, respectively [11]. Therefore, up to 71% and 63% removal efficiencies for COD and BOD, respectively were achieved after the mechanical and pond treatments.

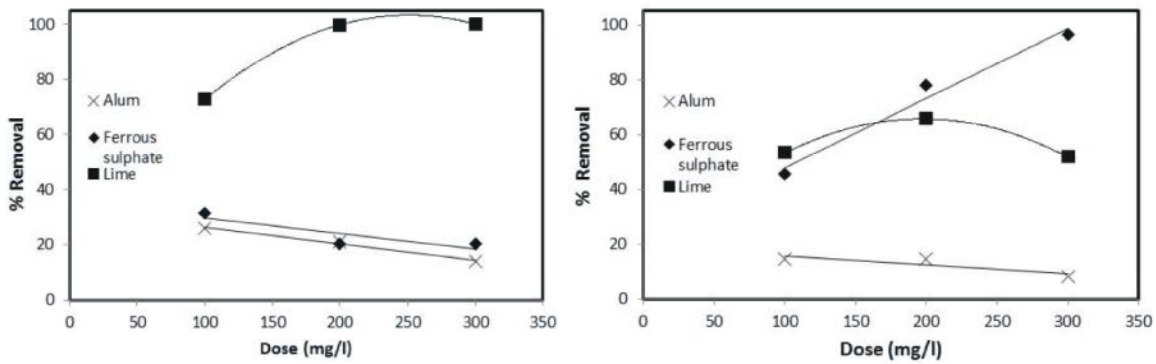
Table 3: Characteristics of the investigated wastewater samples.

Parameter	Sample concentration (mg/l) EW	MW
COD(*dichromate*)	100	750
BOD	40	460
TSS	ND	110
Ni	178	1.960
Cr	24.8	0.110
Pb	--	0.710
Cd	--	0.035

-- not detected

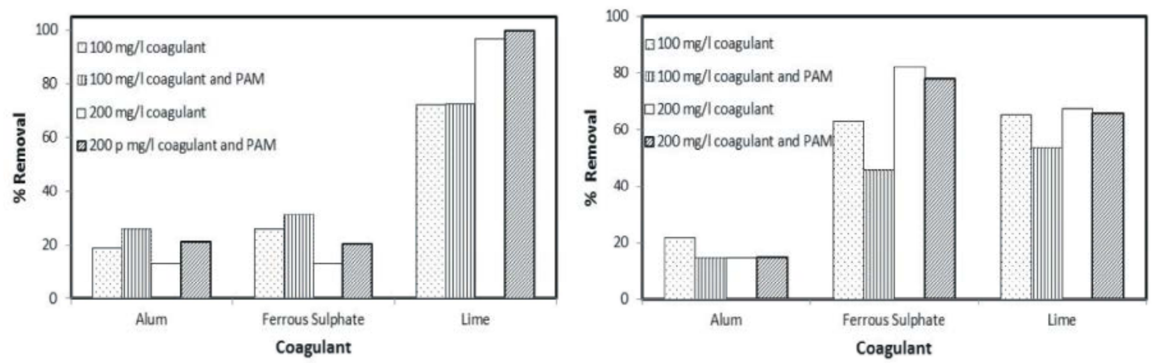
Treatment of Industrial Wastewater Rich in Ni and Cr:

Chemical Treatment: Chemical treatment of industrial electroplating wastewater rich in Ni and Cr sample (EW) was undertaken using different coagulant doses of lime, alum and ferrous sulfate with and without PAM addition. Fig. 2 illustrates the results pertaining to the removal of Ni and Cr using suitable chemical coagulants with PAM addition. It is clear that lime is the most favorable coagulant for the removal of Ni at all the employed doses. However, ferrous sulfate generally exhibits the highest removal efficiencies for Cr and the %removal increases linearly with increasing the coagulant dose. Furthermore, almost all Ni was removed at a lime dose of 200 mg/l while, 96.5% of Cr was removed using 300 mg/l ferrous sulfate. Accordingly, 200 mg/l lime and 300 mg/l ferrous sulfate were chosen to be the optimum doses for Ni and Cr removal, respectively. The effect of PAM on the removal of Ni and Cr at two different coagulant doses of 100 and 200 mg/l is shown in Fig. 3. The results show minor changes in the removal efficiencies of Ni and Cr at the tested conditions.



(a) (b)

Fig. 2: Removal of (a) Ni and (b) Cr from industrial wastewater rich in Ni and Cr using different coagulants and doses with PAM addition.



(a) (b)

Fig. 3: Removal of (a) Ni and (b) Cr from industrial wastewater rich in Ni and Cr using chemical coagulants with and without PAM addition.

Integrated Treatment: A two-stage integrated system involving chemical treatment with PAM addition followed by adsorption onto Calcium-Bentonite was developed. The purpose of the additional adsorption step is to improve the removal efficiencies of Ni and Cr from the wastewater samples that were chemically treated at the optimum coagulation doses (200 mg/l lime for Ni and 300 mg/l ferrous sulfate for Cr). Since Ni was completely removed during the coagulation step, adsorption was conducted only in case of Cr. The overall achieved removal efficiency of Cr using the integrated system was 98%, with 1.5% improvement over the removal obtained by coagulation step.

Treatment of Tenth of Ramadan Mixed Wastewater

Chemical Treatment: Fig. 4 shows the effect of chemical treatment for the mixed wastewater, sample (MW), using different coagulants at various doses with PAM addition on the removal of Ni, Cr, Pb and Cd, respectively. It is clear that almost complete removal of Cr was achieved using all the tested coagulants (alum, lime and ferrous sulfate) at the lowest tested dose(100 mg/l) while, 100% removal of Cd was attained using alum, ferrous sulfate and lime at 300, 200 and 300 mg/l, respectively. Lead was also completely removed using alum and lime at 100 mg/l while, Ni was completely removed using ferrous sulphate and lime at the same dose. In addition, chemical treatment revealed reduction of COD by 50% to 78% depending on coagulant doses (100 - 300 mg/l) with or without PAM addition.

Integrated Treatment: Using the two-staged integrated system, comprising chemical treatment followed by adsorption, almost complete removal of Ni and Cd was achieved from sample (MW) after using alum dose of 100 mg/l. Almost all Pb was removed after using ferrous sulfate dose of 100 mg/l.

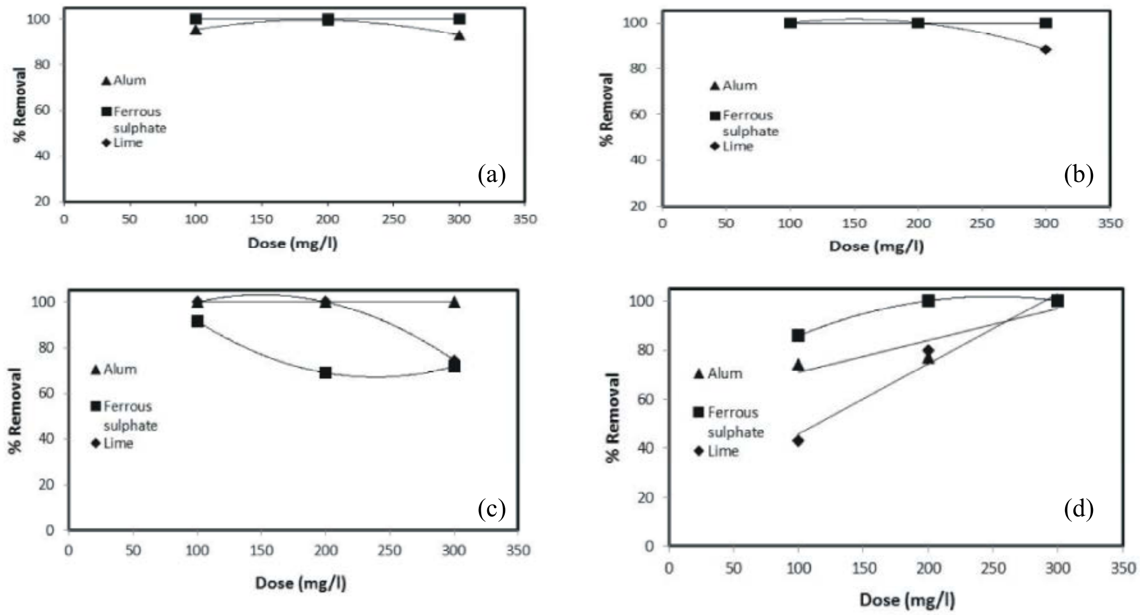


Fig. 4: Removal of (a) Ni, (b) Cr, (c) Pb and (d) Cd from mixed wastewater using different coagulants doses with PAM addition.

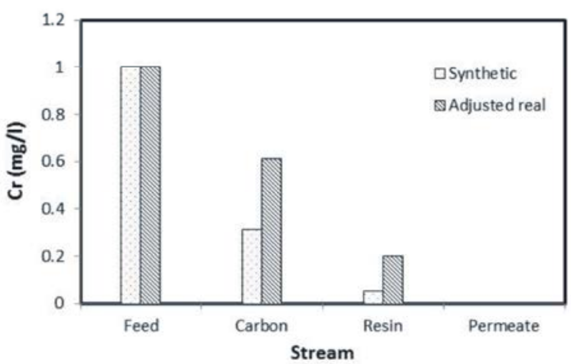


Fig. 5: Removal of Cr from synthetic and adjusted industrial wastewaters using Trisep integrated system.

Trisep Integrated System: Trisep integrated system was used for Ni and Cr removal from both the synthetic and the adjusted real industrial wastewaters. Fig. 5 depicts the removal of Cr from the synthetic wastewater sample (T1) and the adjusted wastewater sample (T2) after each treatment step included in the Trisep integrated system.

The removal of Cr from both T1 and T2 samples decreased gradually after each treatment step. Complete removal of Cr was eventually achieved at the end of the tertiary treatment. Furthermore, the removal of Cr after carbon and resin adsorption was 69% and 95%, respectively from mixed wastewater (T2) as opposed to 39% and 80%, respectively from synthetic sample (T1). In addition, complete removal of Ni was achieved after carbon adsorption.

Proposed Configurations for Trisep Treatment Scheme: Based on reported values for the removal of heavy metals [8, 11-13] as well as the results of Trisep pilot unit, four configurations of tertiary separation systems were suggested for the treatment of Ni and Cr as model ions as shown in Fig. 6. Each configuration was proposed for a particular concentration range in the following manner:

Configuration (1): for relatively high heavy metal concentration (10-20 mg/l) comprises chemical treatment followed by sand filtration then zeolite [14, 15] and finally RO.

Configuration (2): for medium heavy metal concentration (2-10 mg/l) comprises chemical treatment followed by sand filtration then Calcium-Bentonite and finally RO.

Configuration (3): for relatively low heavy metal concentration (0.1-2 mg/l) comprises sand filtration then Calcium-Bentonite and finally zeolite.

The above configurations enable coping with different situations as may be encountered in numerous applications. Moreover and in case of excessive heavy metal loadings (>20 mg/l), a fourth configuration (4)

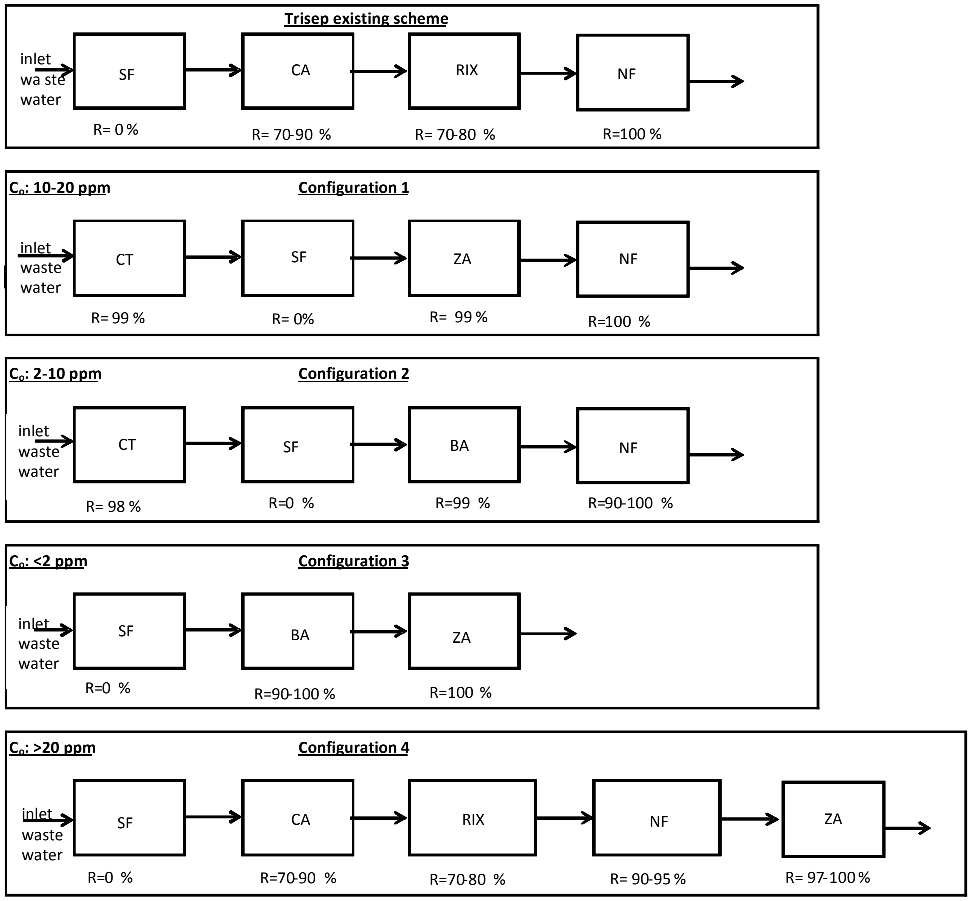


Fig. 6: Proposed system configurations for Trisep technology.

SF: Sand filter	RO: RO membrane (low pressure)
CA: Carbon adsorber	ZA: Zeolite adsorber
CT: Chemical treatment	BA: Calcium-Bentonite adsorber
RIX: Resin ion-exchanger	C_o: Average heavy metal concentration in the inlet wastewater,
	R: Average removal % of Ni and Cr.

may be applied comprising in sequence: sand filtration, carbon adsorption, organic ion exchange resin treatment, zeolite polishing and finally RO. An in-depth financial assessment of the four configurations is currently underway to come up with the pertinent financial indicators for each of the above-mentioned systems.

CONCLUSIONS

An integrated system comprising chemical coagulation followed by adsorption was developed for the treatment of industrial wastewater effluents from the Egyptian industrial city of Tenth of Ramadan. For the wastewater enriched with Ni and Cr, complete removal of Ni was achieved during coagulation using lime at 200 mg/l whereas 98 % of Cr was removed via the integrated system using ferrous sulfate coagulant at 300 mg/l. For the mixed industrial sample, chemical treatment reduced COD by up to 78% and complete removal of Cr was attained using all tested coagulants at 100mg/l. Almost all Pb was completely removed using alum at 100 mg/l. Consecutive adsorption onto Calcium-Bentonite completely removed Ni and Cd. As compared to the pond oxidation treatment method already existing at Tenth of Ramadan, the proposed chemical treatment achieved higher COD reduction (78%) as opposed to (71%) in addition to complete heavy metals removal. The Trisep system proved to be an efficient process for the complete removal of Cr and Ni from both synthetic and real wastewater samples. Four configurations were proposed for the treatment of wastewater with different concentration ranges.

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