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Performance evaluation of an industrial wastewater treatment plant in South-Eastern Tunisia

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ABSTRACT

Heavy metal pollution has become one of the most serious environmental problems today. Heavy metals treatment is of the special concern due to their recalcitrance and persistence in the environment. In this study, four metals (Cr, Cu, Ni, and Zn) found in an industrial wastewater treatment plant in Sfax (South-Eastern Tunisia) were monitored for 10 months in 2012. Metal influent and effluent concentrations of wastewater flocculation process measured via 24-h composite samples were used to determine removal efficiencies. Average influent concentrations varied between 16 ± 13.03 mg/L (Zn) and 167.21 ± 120.06 mg/L (Cr). The flocculation process yielded high removal efficiencies of the studied metals ($\geq 93\%$). Treated wastewaters quality was evaluated according to Tunisian standards for emission into the sewerage system. It was determined that effluent quality in terms of biological oxygen demand, suspending solid, chemical oxygen demand, pH, Cu, and Zn levels were in agreement with standards, but Cr and Ni residual loads were still above the values required by quality criteria.

Keywords: Heavy metals; Industrial wastewater; Water quality

1. Introduction

The accelerated industrialization process in combination with the rapid population growth and agricultural activities have brought about the risk of a pollution index increase in natural environments, such as water, soil, air, etc. [1]. For their multipurpose usage, persistence in the environment, bioaccumula-

tion, and high toxicity, heavy metals are considered among the most hazardous pollutants in the environment [2–5].

The environmental impact of heavy metals is mostly connected to the industrial sources [6–8]. Major industrial sources include surface treatment processes with elements such as lead (Cu), zinc (Zn), nickel (Ni), and chromium (Cr), as well as industrial products that, at the end of their life, are discharged as wastes [9,10].

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Lead can cause central nervous system damage. Lead can also damage the kidney, liver and reproductive system, basic cellular, processes and brain functions. The toxic symptoms are anemia, insomnia, headache, dizziness irritability, muscles weakness, hallucination and renal damages [11]. Zinc is a trace element that is essential for human health. It is important for the physiological functions of living tissues and regulates many biochemical processes. However, too much zinc can cause serious health problems, such as stomach cramps, skin irritations, vomiting, nausea, and anemia [12]. Copper does essential work in animal metabolism. But, the excessive ingestion of copper brings about serious toxicological concerns, such as vomiting, cramps, convulsions, or even death [13]. Nickel exceeding its critical level might result in serious lung and kidney problems aside from gastrointestinal distress, pulmonary fibrosis, and skin dermatitis [14] and it is known that nickel is a human carcinogen. Chromium exists in the aquatic environment mainly in two states: Cr (III) and Cr (VI). In general, Cr (VI) is more toxic than Cr (III). Cr (VI) affects human physiology, accumulates in the food chain, and causes severe health problems ranging from simple skin irritation to lung carcinoma [15].

Due to the increasing anthropogenic contribution of heavy metals, more attention has been devoted to the investigation of these pollutants [16–18].

Nearly all types of water contain heavy metals, many of which result from the natural weathering of the earth's surface [19]. In addition, wastewater used for land irrigation, besides effluent from city sewage and industrial wastewater, could significantly affect water quality. Heavy metals from anthropogenic activities could migrate or infiltrate into aquifers and interact with groundwater [20–22].

In Sfax city, South-Eastern Tunisia, the main source of water or almost the single source is groundwater, since rivers are not available and rainfalls are scarce. The increasing water demand for agricultural, industrial, and domestic purposes in this area under study leads to reuse the wastewater. Wastewater includes industrial emissions, domestic sewage, and drainage water (the unconsumed part of irrigation water). Unfortunately, most industries in that area emit wastes without management. The main purpose of the current study is to achieve the following goals: (i) to determine the levels of some heavy metals, namely Ni, Cr, Cu, and Zn in water samples using atomic absorption spectrophotometer (AAS) through the examination of two sample types including raw influent and treated effluent in an industrial wastewater treatment plant (WTP); (ii) to evaluate the performance of the flocculation process of the studied industrial WTP for removing

heavy metals from wastewater and (iii) to assess the WTP effluent suitability for emissions into the sewerage system.

2. Materials and methods

2.1. Samples collection

Samples were collected from an industrial WTP located in Sfax city, South-Eastern, Tunisia; (Fig. 1) the industrial WTP has been in operation since 1981 and consists of three wash baths: chromic, basic, and acidic, treating simultaneously the chain surface of the company. Depending on its initial pH, each bath will be automatically neutralized by a pump of sulfuric acid or caustic acid to establish a pH between 6.5 and 8.5. After neutralization, discharge from the mentioned baths will be combined in a storage tank for flocculation. Flocculation is the action of polymers to form bridges between the flocs and bind the particles into large agglomerates or clumps. Experiments were conducted using polyacrylamide (Chimifloc 1860 HL) as a flocculant aid. Dose optimization was done and the optimized dose of polyacrylamide (2 mg/L) was applied. The experiment involved slow mixing of wastewater and flocculation at 20 rpm for 180 mn followed by settling and decantation for 210 mn. Once suspended particles are flocculated into larger particles, they can usually be removed or separated by filtration. The treated effluent will be released into the sewerage system while the waste sludge will be recycled.

Composite samples over 24 h were analyzed once in a week, during 2012, from raw influent (before flocculation process) and treated effluent. Fig. 2 shows the sampling sites with two points (W_1 – W_2) for wastewater samples. At each sampling site, three samples were separately taken for a later analysis. After collection, all the samples were collected in brown glass vessels with Teflon caps, precleaned with HNO_3 and deionized water. Samples were transferred to the laboratory within the same day of collection and kept refrigerated (4°C) until analysis (<24 h).

2.2. Sample analysis

Triplicate water samples were analyzed for heavy metals including lead (Cu), nickel (Ni), chromium (Cr), and zinc (Zn) using an AAS (ICE 3000). Briefly, samples were dried at 105°C for 24 h. Subsamples were subsequently digested with 6 mL of HNO_3 (65% analytical grade) and 4 mL of HCl (37% analytical grade) at 160°C. In the second step, samples were allowed to cool for 10 min. After 30 min, the samples were cooled to room temperature and transferred into



Fig. 1. Localization of the study site.

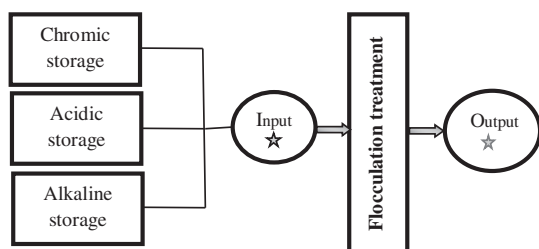


Fig. 2. Sampling sites from the input and the output of the treatment plant.

a 50 mL flask. Finally, the digested samples were filled with distilled water to the 50 mL mark, and used in AAS analysis.

The physico-chemical characteristics of wastewater were validated according to French standard [23]. The chemical oxygen demand (COD) was determined with the digestion reactor using a HACH DR 2010 analyzer. Biological oxygen demand (BOD_5) was determined with the manometric method using an OxiTop respirometer. The pH was measured using pH meter (INOLAB WTW 720). Electrical conductivity (CE) was determined with an electronic conductivity meter (TACUSSEL, CD 6NG) equipped with an immersion measurement probe (cell constant $K_{s/1}=1$ cm). suspending solid (SS) was measured by vacuum filtration of the samples. The removal efficiency (RE) was determined as the percentage of decrease in influent with respect to effluent for each parameter measured.

3. Results and discussion

3.1. Industrial raw wastewater characterization

The total (dissolved + particulate) concentrations of heavy metals determined in raw wastewater samples are presented in (Table 1) along with data for conventional wastewater parameters. The raw wastewater showed a characteristic pH of 2.23 ± 0.4 , and a low suspended solid SS of 14.98 ± 4.42 mg/L, whereas the COD was found to be 662.357 ± 338.673 mg/L and the BOD was determined to be 30.33 ± 18.62 mg/L. Indeed, the EC of the analyzed raw wastewater was

Table 1
Range and mean values of raw wastewater characteristics ($n = 40$)

Raw wastewater characteristics	Range	Mean \pm SD
pH	1.54–3.2	2.23 ± 0.4
SS (mg/L)	5.2–25	14.98 ± 4.42
EC (ms/S 25°C)	8–19.8	13.19 ± 3.05
COD (mg/L)	119–1,300	662.357 ± 338.673
BOD_5 (mg/L)	10–82	30.33 ± 18.62
Ni II (mg/L)	16.2–291	125 ± 59.17
Cr III (mg/L)	4.75–570	167.21 ± 120.06
Cu (mg/L)	2.01–43.45	21.82 ± 13.72
Zn (mg/L)	2–40	16 ± 13.03

greatly high (13.19 ± 3.05 ms/S). It can be attributed to the inorganic mineral charge in the raw influent [24].

Variations in the metals analyzed from raw wastewater in 2012 are given in (Table 1). The results illustrate that the wastewater metal composition is quite variable. The average values of 2012 show that among the metal concentrations studied, Cr presents the highest concentration (167.21 ± 120.06 mg/L) followed by Ni with a concentration of 125 ± 59.17 mg/L. The high levels of those two metals could be attributed to the two incubation phases of the pieces in (Cr) and (Ni). The lead industry has Cu in its effluent, while Ni, Cr, and Zn are attributed to the metal industry [25]. Therefore, the high concentrations of these metals are due to the discharge of the rinsing baths.

3.2. Industrial influent and effluent metal concentrations and removal efficiencies

Monthly variations in the concentrations of the four metals investigated in the industrial influent and effluent within the October–July 2012 period are presented in Fig. 3.

Periodic high influent metal values (~ 152 mg/L Ni, ~ 183 mg/L Cr, ~ 35 mg/L Zn) were measured (Fig. 3). It is possible that metal removal in the metals is replaced with H ions and released under acidic conditions [26].

The effluent values were always lower than the influent values for all metals in all the measurement periods, which indicate effective removal.

The studied company is chiefly designed for the removal of organic and inorganic matter by flocculation process followed by soil filtration. Therefore, metal removal by this system may be regarded as a side benefit, and has been found to be quite variable (between 93 and 96%). Metal contents are listed as $\text{Cu} < \text{Ni} < \text{Zn} < \text{Cr}$ for the 2012 measurement period. Hence, wastewater metal removal may be influenced by their initial influent contents. The relationships between influent metal content and RE (Fig. 3) agree with other findings [27–34], where it was observed that metal removal efficiencies were directly proportional to the metal influent concentrations. Furthermore, metal RE is not only affected by metal ion species and concentration, but also by other conditions such as operating parameters; physical and chemical factors [35].

3.3. Effluent quality

The study of the flocculation system performance included the evaluation of the treated waters quality in comparison to the Tunisian water quality standards for emission into the sewerage system (Table 2). The average values obtained in the effluent for pH, COD, BOD_5 , SS, CE, Cu, and Zn were in agreement with the limits of the Tunisian directives. However, for Cr and

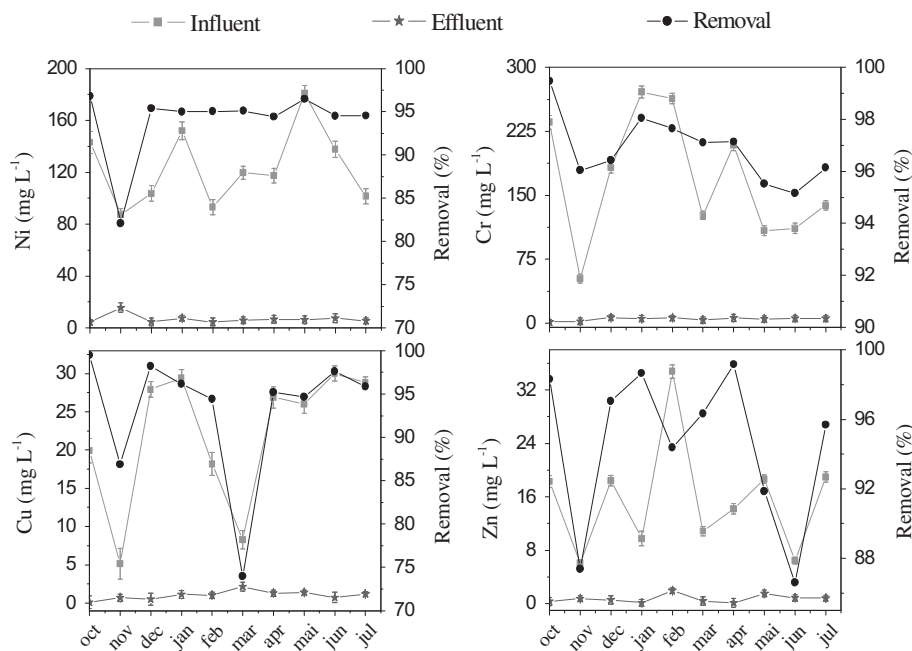


Fig. 3. Monthly variations of industrial influent and effluent metal concentrations and removal efficiencies.

Table 2
Comparison of the average effluent quality to Tunisian standards NT 106.02 (1989)

Parameters	Unit	Treated water quality ^a	Tunisian standards
pH	–	7 ± 0.6	6.5 < pH < 9
BOD ₅	mgO ₂ /L	9.38 ± 4.48	400
COD	mgO ₂ /L	140.3 ± 56.82	1,000
SS	mg/L	4.7 ± 1.4	400
Ni	mg/L	6.86 ± 6.12	2
Zn	mg/L	0.75 ± 0.74	5
Cr	mg/L	4.62 ± 2.35	2
Cu	mg/L	1.05 ± 0.88	1

^aValues are given as a mean of three replications; ±, standard deviations.

Ni, the effluent residual loads were above the values required by standards. The high amounts of Ni and Cr outflow can be partially explained by their relatively elevated concentrations in the raw influent (Table 1). In spite of the advantages cited in the literature, there are inherent limitations to the effectiveness of the flocculation process for industrial wastewater treatment [36]. In some cases, it may not be possible to achieve the desired outflow concentration due to the high natural background levels of the concerned contaminants.

4. Conclusion

In this study, the performance of an industrial WTP was evaluated. Four metals were measured over 10 months. Their contents in the treatment of plant influent are shown to be quite variable. Cr and Ni exhibited the highest concentrations as a result of rinsing bath discharge. The average values showed that Cr, Ni, Cu, and Zn concentrations increased by more than 93% over those measured in 2012. Removal efficiencies were affected by the influent metal contents and the operating parameters. The effluent quality was still compliant with the Tunisian standards for the emission into the sewerage system in terms of BOD₅, SS, CE, COD, pH, Cu, and Zn levels. Despite the high removal of Cr and Ni, 96 and 93%, respectively, their residual loads greatly exceeded the required standards. The treatment of these metals may be achieved through other treatment processes, such as ion-exchange processes, or by shifting soil with a cheap local material i.e. clay minerals for a better filtration. Other treatment approaches, like adsorption on specific media or chemical reactions, are often advised for metals reduction.

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