Environmental Engineering and Management Journal *June 2021, Vol. 20, No. 6, 995-1002*
http://www.eemj.icpm.tuiasi.ro/; http://www.eemj.eu

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REMOVAL EFFICIENCY OF HEAVY METALS BY A BIOLOGICAL WASTEWATER TREATMENT PLANT AND THEIR POTENTIAL RISKS TO HUMAN HEALTH

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Abstract

The main purpose of this research was to study the fate and removal of heavy metals by a biological wastewater treatment plant. The levels of heavy metals were compared in wastewater and sludge before and after treatment. The content of heavy metals wastewater and sludge was determined by inductively coupled plasma spectrometry (ICP-OES). Some of the metals were found to be present in trace amounts, while others were dispersed over a wide range of concentrations and were sometimes below the limit of detection. They occurred in the following order: Fe > Zn > Cu > Mn > Ba > Pb > Cr > As > Co > Ni > Cd > Hg. The reduction in heavy metal concentrations was in direct proportionality to their starting levels in the influent wastewater. The heavy metal concentration was, in ascending order, proportional to the content of the influent: Ba < Co < Mn < Pb < Cu < Zn < As < Ni < Cr < Fe < Cd < Hg. These metals concentrated in the sludge and accumulated after treatment. Concentrations of heavy metals in treated sludge were found to meet standards for agricultural land application. Values for lifetime cancer risk due to exposure to heavy metals in sludge samples were also estimated and it ranged from 4.42E-07 to 5.89E-04 for adults and children. The number of people suspected of having cancer due to exposure to sludge is between 6 and 44 in 10 million.

Keywords: health risk assessment, heavy metals, removal, wastewater treatment plant

Received: April, 2020; Revised final: July, 2020; Accepted: October, 2020; Published in final edited form: June, 2021

1. Introduction

The contamination, particularly aquatic, by many micropollutants (MPs) is one of the major environmental concerns. Indeed, many micropollutants from human activity, particularly in urban areas, are rejected in the water masses, degrading their quality and disrupting their good ecological functioning. The presence of these substances in wastewater is one of the major causes of pollution of water and soil (Luo et al., 2014).

Among these micropollutants there are heavy metals who are harmful to humans and environment (Chipasa, 2003; Drozdova et al., 2019). They may be absorbed and accumulated in the body and cause serious health effects such as cancer, damage to organs, to the nervous system and, in extreme cases, death. They also reduce growth and development (Mishra et al., 2019). Heavy metals (HMs) are generally defined as elements having a density greater than 5 g /cm^3 (Rahman and Singh, 2018). The majority of the elements that fall into this category are toxic substances and well-known carcinogens that are highly soluble in water. Heavy metals are considered to be the following: copper, cadmium, gold, silver, zinc, mercury, lead, chromium, iron, nickel, tin, arsenic, selenium, cobalt, manganese, molybdenum, and aluminum (Chaemiso and Nefo, 2019). Since these metals are highly toxic even in small quantities,

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their removal from wastewater has recently been the subject of considerable interest due to strict legislation. The removal of heavy metals from wastewater can be achieved by various treatment options, including unit operations such as chemical precipitation, coagulation, complexation, activated carbon adsorption, ion exchange, solvent extraction, foam flotation, electroplating, and cementing. The accumulation of these metals in wastewater depends on many local factors such as the type of industries in the region, the way of life of people and their awareness of the environmental consequences of careless waste disposal.

One of the main issues related to mineral micropollutants in sanitation is their release into the environment via domestic wastewater treatment plants (WWTP) effluents (Chipasa, 2003). The WWTPs are considered as the intermediary connecting between the urban environment and the natural environment, one of the main stakes of the micropollutants is their rejections in the natural envi-ronment by this intermediary (Rogers, 1996). These releases have been considered an important source of introduction into the environment and their contribution to environmental contamination has been demonstrated. This is why regulations have been put in place to limit their presence in the environment.

Health risk assessment (HRA) is usually used to estimate the risk of human exposure to certain contaminants in a known quantity. There are three main routes by which human exposure to the impacts of heavy metals can occur, such as (i) the direct oral ingestion of heavy metal parti-cles, (ii) inhalation of heavy metal particles through the mouth and nose and (iii) dermal absorp-tion of heavy metal particles on exposed skin (Kusin et al., 2018).

In order to face the challenges of escalating food demand, the reuse of wastewater in the irrigation of agricultural land is a realistic alternative to increase water resources in Morocco. De-watered sewage sludge was spread on agricultural land in Morocco. The sludge contains varying concentrations of heavy metals, including Cd, Pb, Ni, Cr, Cu, Fe and other trace elements, which can pose serious risks to animal health and the human food chain, this is why regulations have been set up to prevent the contamination of living beings by these elements (Hussein et al., 2005).

This study presents the results of an 18 months survey on the accumulation and elimination of certain heavy metals (Cu, Zn, Fe, Mn, Cd, Pb, As, Ni, Ba, Cr, Co and Hg) by a biological wastewater treatment system illustrated by Al-Hoceima wastewater treatment plant (WWTP). The objectives of the study were: (1) comparing the concentration of heavy metals in raw and treated wastewater, (2) evaluation of the heavy metal concentration in sludge before and after treatment, and determine if the sludge removed is suitable for agriculture use, and (3) assessment of the total risk of cancer due to exposure to heavy metals in sludge samples.

2. Material and methods

2.1. Description of Al-Hoceima wastewater treatment plant

The city of Al-Hoceima is located on the Mediterranean coast north of Morocco, while WWTP of Al-Hoceima city is located in the northwest of the city positioned over an area of 4 ha (Fig. 1). It was put in operation in 1996. In order to follow the evolution of the urbanization and population, the station was rehabilitated in 2011 in order to increase its capacity from a flow of 4800 m^3/d to 9600 m^3/d. The purification process implemented is a biological treatment of activated sludge at low charge. The main objective is to reduce the level of pollution from industrial and municipal wastewater before discharging it into the environment. Wastewater treatment starts with the removal of coarse particles, oils, greases and sands (pretreatment) (Fig. 2).

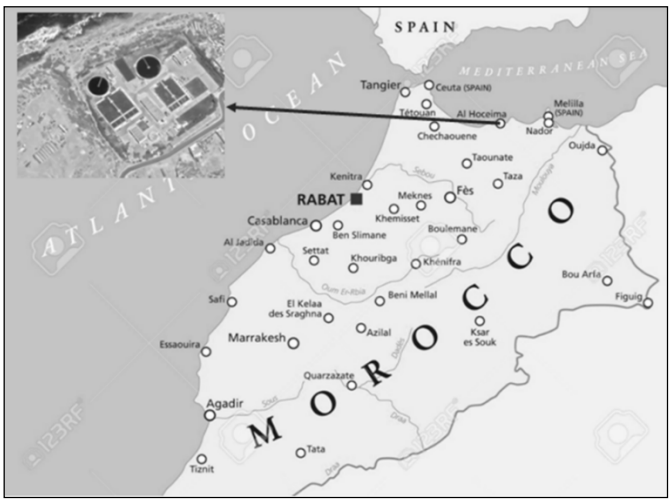

Fig. 1. Location of the WWTP of Al-Hoceima city
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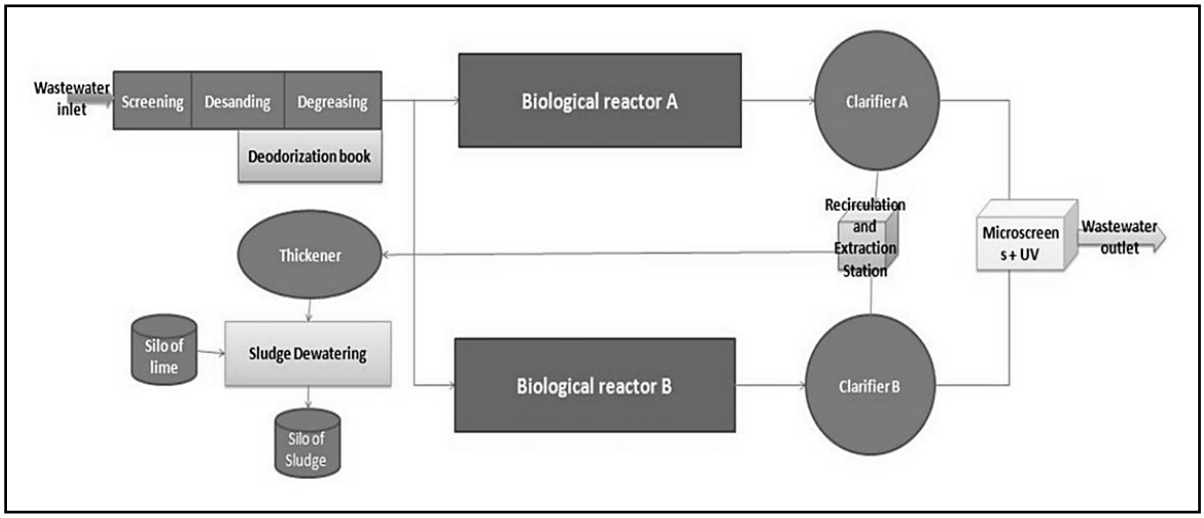

Fig. 2. Design of the Al-Hoceima city wastewater treatment plant
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The pre-treated waters are then directed to two biological reactors running in parallel and containing successively an anaerobic zone, an anoxic zone and an aerobic zone where the elimination processes take place. Then, the treated water is first subjected to microfiltration for the final removal of the remaining Total Suspended Solids (TSS), followed by ultraviolet (UV) disinfection to kill bacteria, viruses and parasites (tertiary treatment).

The biological sludge from the treatment process is submitted to a mechanical thickening process using four rotary filters, followed by a dewatering operation on two centrifuges operating in parallel. After dewatering, the sludge is limed to a dryness of 25% before being dumped in the Al-Hoceima landfill (Dimane et al., 2016).

2.2. Sample collection and analysis

Samples of wastewater and sludge were collected at four different points in the station, including the influent (raw wastewater, RW), effluent (treated wastewater, TW), activated sludge from the recirculation stream (excess sludge, ES) and dewatered sludge (final sludge, FS). Water volumes were collected using refrigerated (4°C) auto samplers, and sludge samples were collected manually.

Samples from different stages of purification were transported in polyethylene containers. At the time of collection, some samples were acidified. Other samples that did not require preservation before analysis being were stored at 4°C.

For heavy metal analysis, 100 ml of well-mixed wastewater sample was heated on a hot plate at 85 °C until the sample volume was reduced to 20 ml. The sample was then digested and allowed to cool. Afterwards, it was filtered to separate insoluble and suspended matter. The filtrate was quantitatively transferred to a 50 ml volumetric flask and diluted to volume with purified water and mixed to be ready for analysis.

Limit of detection for heavy metals in wastewater and sludge samples are presented in Table 1. For sludge samples, 5.0 g dry weight was mineralized and treated as described above. The prepared mineralized samples were analyzed. To determine the amount of heavy metals present in the samples an Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES Agilent 730) was used.

Table 1. Limit of detection for heavy metals in wastewater and sludge samples

Heavy metals	***Limit of Detection in wastewater (µg/L)***	***Limit of Detection in sludge (mg/kg)***
Cu	0.0010	0.004
Zn	0.0020	0.003
Fe	0.0060	0.004
Mn	0.0001	0.004
Cd	0.0002	0.002
Pb	0.0020	0.02
As	0.0010	0.004
Ni	0.0002	0.004
Ba	0.0020	0.004
Cr	0.0005	0.004
Co	0.0025	0.004
Hg	0.0001	0.004

Many parameters were monitored every month over an 18-months period: hydrogen potential (pH), temperature, suspended solids (SS), dissolved oxygen, electrical conductivity (EC), chemical oxygen demand (COD), biological oxygen demand after five days (BOD_5), ammonium, nitrite, nitrate, total nitrogen (TN), total phosphorus (TP). The physico-chemical parameters (T, EC, pH, dissolved oxygen) were measured in situ. TSS were filtered through a 0.45 micrometer porous membrane and dried at 105°C. COD was analyzed by excess oxidation with potassium di-chromate under acidic conditions at 150°C (standard method) and BOD_5 was evaluated by the method gauge, based on OXITOPs methods.

N compounds were measured using a portable spectrophotometer DOTAL ogying HACH DR / 4000. The determination of nitrate was performed according to method 8507. Nitrate is reduced to nitrite under acidic conditions and the measurement was carried out using a Dotalogying HACH DR / 4000 portable spectrophotometer. The determination of ammonium ions is based on the reaction with chlorine under alkaline conditions to form monochloramine. For total phosphorus (TP), the determination is carried out in one step consisting in digesting and oxidizing all forms of phosphorus with potassium persulphate in an acidic medium under pressure at 121°C.

2.3. Potential human health risk assessment from exposure to HMs from treated sludge

In particular, the health risks from ingestion, inhalation and dermal contact in adults and children can be predicted by estimating the chronic daily intake (CDI) (mg/kg/day). In this study, the following equations (Eqs. 1-3) were used to assess the potential risk to human health of heavy metals present in WWTPs sludge samples (Chonokhuu et al., 2019; Diami et al., 2016; Li et al., 2015).

$$CDI(ing) = \frac{Ci \times IngR \times EF \times ED \times CF}{BW \times AT} \quad (1)$$

$$CDI(inh) = \frac{Ci \times IngR \times EF \times ED}{PFE \times BW \times AT} \quad (2)$$

$$CDI(der) = \frac{Ci \times SA \times AF \times ABS \times EF \times ED \times CF}{BW \times AT} \quad (3)$$

Table 2 shows the input parameters for the risk estimates.

Table 2. Exposure factors used in CDI estimation

Symbol	***Parameter***	***Unit***	***Value***
Ci	Concentration	mg/kg	---
IngR	Ingestion rate	mg/day	Adult: 100 Children: 200
InhR	Inhalation rate	mg/day	20
EF	Exposure frequency	days/year	350 days/year
CF	Conversion factor	kg/mg	10^{-6}
ED	Exposure duration	years	Adult: 24 Children: 6
BW	Body weight	kg	Adult: 70 Children: 15
AT	Averaging time	day	25550 days
PFE	Particle emission factor	m^3/kg	1.36×10^9
SA	surface area	cm^2	5700
AF	Adherence factor	mg/cm^2	0.07
ABS	Dermal absorption factor	---	0.001

The Hazard Index (*HI*) representing the cumulative non-carcinogenic risk is estimated by summing all hazard quotients (*HQ*) as expressed in Eqs. (4-5):

$$HQ = \frac{CDI}{RfD} \quad (4)$$

$$HI = \sum HQ = HQ(ing) + HQ(inh) + HQ(der) \quad (5)$$

USEPA (2011) states that the reference dose (*RfD*) in equation refers to the reference dose for the calculation of the HRA, and the values of the reference dose for each element are different (Table 3).

Table 2. Reference dose (*RfD*) values of heavy metals (USEPA, 2011)

Heavy metals	***RfD (mg/kg/day)***
Cu	0.0371
Co	0.0200
Fe	0.7000
Pb	0.0035
Zn	0.3000
Cr	0.0030
Cd	0.0010
Ni	0.0008
As	0.0003
Hg	0.0004

When the *HI* value is less than 1 (*HI* < 1), there is no significant risk of non-cancerous consequences. And if the *HI* value is greater than 1 (*HI* > 1), there's a significant non-carcinogenic risk effects (Wang et al., 1999).

In this study, the heavy metals evaluated are Cu, Zn, Fe, Cd, Pb, As, Ni, Cr, Co and Hg. According to IRIS (2011), Cd, Cr, Pb and As are classified as possibly carcinogenic, while Fe, Zn, Cu, Ni and Co are non-carcinogenic. Cancer risk (*CRI*) is calculated using Eq. (6), by estimating the total value of cancer risks for each exposure pathways (Eq. 7). The cancer slope factor (*CSF*) values for Cd, Cr, Pb and As are 6.3, 0.5, 0.0085 and 1.5 mg/kg/day (USEPA, 2011). The accepted threshold value for cancer risk is 1.0×10^{-4}, while the tolerable CSF for regulatory purposes is in the range of 1.0E-06 to 1.0E-04 (USEPA, 2002).

$$CRI = CDI \times CSF \quad (6)$$

$$\sum CRI = LCR = CRI(ing) + CRI(inh) + CRI(der) \quad (7)$$

3. Results and discussion

3.1. Performance of the wastewater treatment plant

Physical and chemical characteristics of raw and treated wastewater are summarized in Table 4. During this study, the WWTP operated at rated capacity. The treatment removed approximately 96% of the TSS, 95% of the chemical oxygen demand (COD), 98% of the biological oxygen demand (BOD_5), 94% of the total N, 98% of the NH^{4+}, 64% of the NO^{2-} and 46% of the total P.

3.2. Comparison of heavy metal contents in raw and treated wastewater

The heavy metal content of the influent and effluent was compared to assess the removal of heavy

metals from the influent wastewater by the biological treatment system. Samples were monthly collected and analyzed for an 18 months period. The median values of this period in effluent and influent streams are shown in Table 5.

Based on the comparison with other studies (Balmér, 2001, Chipasa, 2003, Karvelas et al., 2003), it is clear that the reported concentrations of these metals are dispersed over a wide range and the results found in this study are perfectly comparable with these data. Indeed, according to Rule et al. (2006), plumbing systems and pipes are the main source of metals in domestic wastewater. Nevertheless, in addition to releases caused by human activities, wastewater runoff and the geochemical composition of the rocks themselves can play an important role in the presence of these substances. It is clear that the concentrations of some heavy metals, such as Cd, Ni, Cr, Co and Hg, are practically at low levels, while others, such as Mn, and Pb, may show some peak concentration. Cu is always the most abundant of the heavy metals, while Fe, Zn are clearly predominant and can be very high. The occurrence of As, a non-metal, is generally low, but due to its toxicity, a special attention should be paid to it. The removal of heavy metals is achieved in both primary treatment and secondary biological treatment (Oliver and Cosgrove, 1974). Biological wastewater treatment plants are mainly designed for the removal of organic matter by micro-organisms from activated sludge (Chipasa, 2003). Thus, removing heavy metals from these systems can be classified as a secondary benefit, and was found to be highly variable.

The removal of heavy metals from activated sludge is known to be dependent on dissolved organic matter and pH, with removal efficiency increasing with pH until the metals precipitate as hydroxides (Wang et al., 1999). Removal efficiencies (*RE* %) of heavy metals during the treatment process in WWTPs were determined using the standard equation (Eq. 8):

$$RE\% = \frac{Cinf - Ceff}{Cinf} \quad (8)$$

where: *Cinf* and *Ceff* concentration in the influent and the effluent.

A total removal efficiency of all the HMs compounds studied ranged between 25% and 83%. Fig. 3 shows a medium value of the removal efficiency during the period of our study. According to literate reports (Carletti et al., 2008; Karvelas et al., 2003), it seems that heavy metals are generally removed with high efficiency and in full accordance with this previous experiences. In particular, the effectiveness of the removal follows the order: Co < Cr < As < Ni < Ba < Pb < Cd < Cu < Mn < Fe < Zn < Hg in accordance with the data in the literature. During wastewater treatment, heavy metals are absorbed into the sludge.

3.3. Comparison of heavy metal content in untreated and treated sludge

Sludge samples used in this study are sludge produced at the Al-Hoceima wastewater treatment plant. All twelve searched metals appeared in sludge samples.

Table 3. Physical and chemical characteristics of raw and treated wastewater

Parameters	***Unit***	***Raw wastewater***	***Treated wastewater***	***Discharge limit values***
Temperature	°C	22.02 ± 1.19	23.64 ± 1.45	30
pH	----	7.89 ± 0.078	7.35 ± 0.05	5.5 - 8.5
Electrical Conductivity	µS/cm	2729.04 ± 252.36	2240 ± 187.71	2700
TSS	mg/L	353 ± 52	13.43 ± 0.32	150
COD	mg O_2/L	844.28 ± 69.66	36.92 ± 5.36	250
BOD	mg O_2/L	569.27 ± 15.60	10.09 ± 1.54	120
Total Nitrogen	mg/L	85.18 ± 7.85	4.77 ± 0.54	40
Ammonium	mg/L	44.92 ± 2.30	0.3 ± 0.03	---
Nitrate	mg/L	1.80 ± 0.36	4.79 ± 0.48	---
Nitrite	mg/L	0.35 ± 0.03	0.12 ± 0.01	---
Total phosphorus	mg/L	8.94 ± 0.35	4.74 ± 0.57	15

Table 4. Variations in heavy metals before and after treatment in wastewater and sludge

Heavy metals	***Wastewater in µg/L***		***Sludge in mg/kg dw***		
	Influent	***Effluent***	***Untreated***	***Treated***	***Limit values for agriculture use***
Cu	298.21 ± 73.69	74.16 ± 21.08	219.12 ± 79.65	122.10 ± 30.09	1000-1750
Zn	389.34 ± 89.60	63.32 ± 17.41	290.31 ± 68.02	214.21 ± 62.58	2500-4000
Fe	844.63 ± 102.04	143.09 ± 41.02	484.24 ± 128.04	398.17 ± 101.35	---
Mn	142.12 ± 49.02	34.25 ± 11.31	102.38 ± 39.61	98.03 ± 45.49	---
Cd	4.65 ± 1.10	1.30 ± 0.40	1,60 ± 0.43	0.67 ± 0.10	20-40
Pb	28.17 ± 5.90	8.02 ± 1.93	53.39 ± 11.21	45.20 ± 16.39	750-1200
As	8.12 ± 3.19	4.60 ± 0.90	75.61 ± 21.35	42.29 ± 20.27	45
Ni	5.70 ± 2.04	2.00 ± 0.93	23.32 ± 9.18	18.40 ± 6.94	300-400
Ba	97.41 ± 28.37	34.14 ± 11.37	73.37 ± 23.42	61.20 ± 30.53	---
Cr	7.90 ± 2.54	5.20 ± 2.05	69.52 ± 19.96	19.95 ± 9.13	1000
Co	7.70 ± 1.98	5.10 ± 1.84	89.51 ± 32.47	38.32 ± 19.83	---
Hg	1.20 ± 0.20	0.20 ± 0.12	1.80 ± 0.40	1.05 ± 0.30	16-25

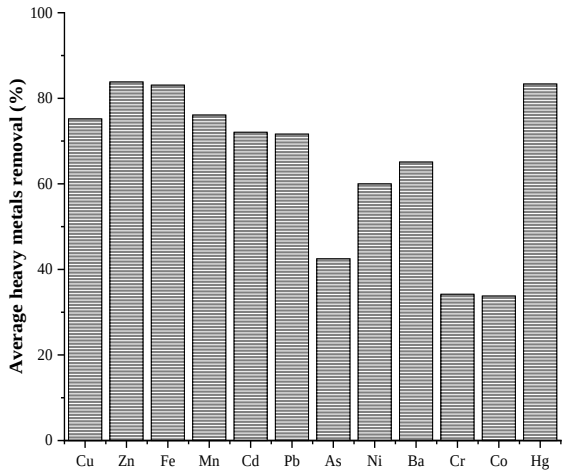

Fig. 3. Average heavy metal removal efficiencies from influent wastewater

The heavy metals in sludge are present in the form of: metallic precipitates in the sludge flocks; soluble metal and bi-opolymer complexes; soluble metal accumulated in microbial cells; and soluble metal ions (Brown and Lester, 1979).

All heavy metals in influent sludge were detected at concentrations ranging from 1.6 mg/kg dry weight (Cd) to about 484 mg/kg dry weight (Fe), and in effluent sludge from 0.67 mg/kg dry weight (Cd) to nearly 398 mg/kg dry weight (Fe) (medium values during 18 months) (Table 5), with the medium removal efficiencies during our study period going from 5% (Mn) to 66% (Co) (Fig. 4).

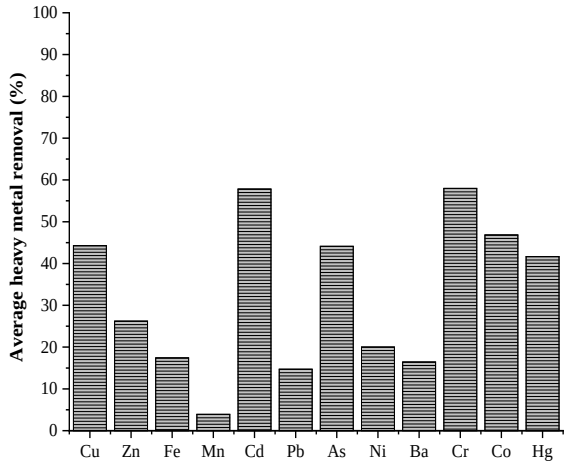

Fig. 4. Average heavy metal removal efficiencies from influent sludge

The limits set by various countries for heavy metals in sewage sludge for agriculture are shown by (Holm et al., 2002; Iranpour et al., 2004). As it can be seen, the sludge produced in the Al-Hoceima sewage treatment plant meets the requirements set by legislation for all heavy metals and could therefore is recommended for use in agriculture (Table 5) (Inglezakis et al., 2014). Heavy metal accumulation and removal is affected by the treatment system itself.

When calculating the removal efficiency, for example, only the heavy metal content of the influent stream is considered relative to that of the effluent. The biological treatment system is highly supercharged by heavy metals contained in the returned streams, i.e. recycled activated sludge and returned wastewater (Chipasa, 2003).

Four mechanisms appear to influence the accumulation and transport of heavy metals in the treatment system: (i) bioaccumulation, a process of active interaction of heavy metals with microbial cells by which metal ions enter the cells; (ii) biosorption, defined as the total of all passive interactions of microbial cell walls with metal ions, in this case, heavy metals are absorbed onto the phosphate and groups of lipids, proteins and polysaccharides present on the cell surface); (iii) the solubility of heavy metals, i.e. occurrence of soluble metal ions in wastewater and the liquid fraction of sludge; and (iiii) sorption to extracellular biopolymers and wastewater particles (Ahalya et al., 2003).

Heavy metal transport and absorption from activated sludge depends primarily on these physical, chemical and biological mechanisms. The levels of heavy metals found in treated wastewater and sludge effluent vary depending on the design of the wastewater treatment system and the characteristics of the influent wastewater. Further researches are needed on the effects of heavy metal levels in return flows on heavy metal levels in influent and effluent waters.

3.4. Potential human health risk

Several metals are toxic and constantly destroy human health, affecting human organs. They are therefore considered to be the pollutants that cause carcinogens. Eqs. (1-7) are used to calculate the health risk assessment. Tables 6-7 show results of exposure to heavy metals in the sludge samples studied with three pathways (ingestion, dermal and inhalation). The hazard quotient for the non-carcinogenic risk by three routes is in the following order: soil ingestion > skin contact > inhalation. Of the three pathways, the contribution of soil ingestion to the total non-carcinogenic (*HI*) risk is the highest, demonstrating that soil ingestion is the major route of exposure to human health risk. There was a similar pattern of the three routes for adults as for children.

The *HI* values are shown in the following order, as shown in Table 6: Ni > Pb > Cr > As > Cu > Hg > Zn > Cd > Fe > Co for both adults and children. For children, *HI* values range from 1.10E-05 to 2.53E-03, while *HI* values for adults range from 4.2E-06 to 1.09E-03. Children generally suffer higher non-cancer risks than adults in all aspects of ingesting heavy metals and metalloids, which indicates that children are more sensitive to environmental pollution. There is a potential risk that the public may have an influence on non-carcinogenic if *HI* values are higher than 1. Clearly, the *HIs* for children and adults are well below 1.

Table 5. Chronic daily intake (*CDI*), hazard quotient (*HQ*) and cumulative hazard index (*HI*) for non-carcinogenic risk

Adults							
Metal element	***CDI (ing)***	***CDI (inh)***	***CDI (der)***	***HQ (ing)***	***HQ (inh)***	***HQ (der)***	***HI***
Cu	5.73E-06	8.43E-09	2.28E-08	1.54E-04	2.27E-07	6.16E-07	1.55E-04
Zn	1.05E-05	1.48E-08	4.01E-08	3.35E-05	4.93E-08	1.33E-07	3.37E-05
Fe	1.86E-05	2.75E-08	7.45E-08	2.67E-05	3.93E-08	1.06E-07	2.68E-05
Cd	3.17E-08	4.66E-11	1.26E-10	3.17E-05	4.66E-08	1.26E-07	3.19E-05
Pb	2.12E-06	3.12E-09	8.47E-09	6.07E-04	8.92E-07	2.42E-06	6.10E-04
As	6.10E-08	8.98E-11	2.43E-10	2.04E-04	2.99E-07	8.12E-07	2.05E-04
Ni	8.64E-07	1.27E-09	3.44E-09	1.08E-03	1.59E-06	4.31E-06	1.09E-03
Cr	8.78E-07	1.29E-09	3.50E-09	2.93E-04	4.31E-07	1.16E-06	2.94E-04
Co	9.39E-08	1.38E-10	3.74E-10	4.70E-06	6.91E-09	1.87E-08	4.72E-06
Hg	4.93E-08	7.25E-11	1.96E-10	1.23E-04	1.81E-07	4.91E-07	1.24E-04
Children							
Metal element	***CDI (ing)***	***CDI (inh)***	***CDI (der)***	***HQ (ing)***	***HQ (inh)***	***HQ (der)***	***HI***
Cu	1.33E-05	9.83E-09	2.667E-08	3.60E-04	2.65E-07	7.19E-07	3.61E-04
Zn	2.34E-05	1.72E-08	4.679E-08	7.82E-05	5.75E-08	1.56E-07	7.84E-05
Fe	4.36E-05	3.21E-08	8.701E-08	6.23E-05	4.58E-08	1.24E-07	6.25E-05
Cd	7.39E-08	5.44E-11	1.476E-10	7.40E-05	5.44E-08	1.48E-07	7.42E-05
Pb	4.95E-06	3.64E-09	9.882E-09	1.42E-03	1.04E-06	2.82E-06	1.42E-03
As	1.42E-07	1.05E-10	2.842E-10	4.75E-04	3.49E-07	9.47E-07	4.76E-04
Ni	2.01E-06	1.48E-09	4.023E-09	2.52E-03	1.85E-06	5.03E-06	2.53E-03
Cr	2.04E-06	1.51E-09	4.088E-09	6.83E-04	5.02E-07	1.36E-06	6.85E-04
Co	2.19E-07	1.61E-10	4.373E-10	1.10E-05	8.06E-09	2.19E-08	1.10E-05
Hg	1.15E-07	8.46E-11	2.296E-10	2.88E-04	2.12E-07	5.74E-07	2.88E-04

Table 6. Carcinogenic risk for different exposure pathways for adults and children

Metal	***Adults***				***Children***			
	CRI (ing)	***CRI (inh)***	***CRI (der)***	***LCR***	***CRI (ing)***	***CRI (inh)***	***CRI (der)***	***LCR***
Cd	1.99E-07	2.94E-10	7.97E-10	2.01E-07	1.17E-08	8.63E-12	2.34E-11	1.18E-08
Pb	1.80E-08	2.65E-11	7.20E-11	1.81E-08	5.83E-04	4.28E-07	1.16E-06	5.89E-04
As	9.15E-08	1.35E-10	3.65E-10	9.21E-08	9.49E-08	6.98E-11	1.89E-10	9.52E-08
Cr	4.39E-07	6.46E-10	1.75E-09	4.42E-07	4.09E-06	3.01E-09	8.18E-09	4.11E-06

In addition, the values for carcinogenic risk for children and adults are illustrated in Table 7. None of Cu, Zn, Ni, Co and Hg is presented as there were no carcinogenic slope factors for these substances. The lifetime cancer risk has a similar trend to the *HI* values. Risk of carcinogenicity decreases as follows: soil ingestion > skin contact > inhalation. In the case of children and adults, As, Pb and Cr pose a greater carcinogenic risk, and the *LCR* values for Cr range from 1.18E-08 to 5.84E-04 (for children) and from 1.81E-08 to 4.42E-07 (for adults).

The total estimated cancer risks associated with exposure to sludge samples - HMs were considered acceptable. Even in the worst-case scenario, the estimated cancer risks for adults and children are within the acceptable range of excess cancer risk specified (1.0E-06 to 1.0E-04) by the USEPA.

4. Conclusions

An evaluation of the level of heavy metal removal from wastewater by a biological wastewater treatment system was attempted in this study. In addition, the heavy metal contents of the untreated and treated sludge were compared. Conclusions of the study are as presented below:

- The heavy metal content of the influent wastewater was highly variable. The majority of heavy metals were present in trace amounts in wastewater, and the occurrence of metals was Fe > Zn > Cu > Mn > Ba > Pb > Cr > As > Co > Ni > Cd > Hg.
- Heavy metals removal from wastewater is affected by their initial content in the influent. Therefore, the removal of heavy metals is directly related to the concentrations of the influent heavy metals. They have been effectively removed by wastewater treatment plants. The efficiency of removal was in the following order: Co < Cr < As < Ni < Ba < Pb < Cd < Cu < Mn < Fe < Zn < Hg and was in good agreement with the literature.
- The metals are accumulated in the activated sludge and, once stabilized, some problems may occur. The sludge produced in the Al-Hoceima WWTP meets the requirements set by legislation for all heavy metals and could therefore be recommended for use in agriculture.
- The biological wastewater treatment system studied was found to meet the compliance limits for treated wastewater.
- The Estimated Total Cancer Risk from exposure to heavy metals in the sludge samples studied ranged from 4.42E-07 for adults to 5.89E-04

for children. Approximately 6 to 44 in 10 million people are suspected of developing cancer from exposure to sludge from sewage treatment plants.

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