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OCCURRENCE, SEASONAL CHANGES AND REMOVAL EFFICIENCY ASSESSMENT OF HEAVY METALS IN URBAN WASTEWATER TREATMENT PLANT

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ABSTRACT

The impact of heavy metals in the aquatic environment expanding day after day, especially with the increase of industrialization and urban development. In this study, the presence, seasonal changes, and removal efficiency of thirteen heavy metals (As, Se, Al, Ag, Sb, Ba, Hg, Cd, Pb, Mn, Cr, Fe, and Ni) assessed by using inductively coupled plasma mass spectrometry (ICP-MS) in both influent and effluent of Saruhanli wastewater treatment plant in Manisa city, western Turkey, operated for urban wastewater processing. Samples collected once sample per month from April 2018 to February 2019. According to the results, all metals founded in both influent and effluent samples of WWTP except Ag and Al not founded in the effluent, the concentration of metals in influent was high ranged from 0.096 µg. L^{-1} for Ag to 38151.867 µg/L for Fe. The highest removal efficiency was 100%, 100%, 99 %, 99.5% for Ag, Al, Fe, Ni respectively. While the lowest removal percentage was 11%, 19.35%, 27.87% for (Ag, Sb, and As) respectively. Seasonal and yearly differences were also taken in the consideration, (As and Sb) was low in all-seasons during the sampling period.

Contribution/ Originality: The pollution of water environments by heavy metals has been a primary issue in different countries. The paper contributes to measure the Occurrence, seasonal changes and Removal efficiency of heavy metal which resemble first time records in Saruhanli district belong to Manisa city.

1. INTRODUCTION

In recent years, the pollution with heavy metals consider one of the most serious problems which cause ecotoxicology in all over the world [1-4] and further induce environment costs [5] also arising day after day [6]. The increasing contamination with heavy metal in the water environments has started to attract the attention of many researchers [1] because of this mater attached directly with public health concern, their toxicity in relatively very low concentrations and their long persistence in the nature [1, 7].

Industrial and urban Wastewater contains many chemical and biological materials, chemical material either organic or inorganic. The most dangerous inorganics are heavy metals, the prevalence of heavy metals in wastewater, especially in effluent part which produce different degrees of pollution hazards and further induce environment costs [5]. Thus, urgent removal of those metals from water systems consider very important [8].

Despite it is extremely challenging to treat wastewater containing large number of heavy metals via one-step treatment, recent researches has been accomplished to apply efficient methods with minimum use of chemicals and without impact on the environment [9]. Nowadays, classic wastewater treatment methods are not efficient for removal toxicity of heavy metals. So, a new technique must be used for overcoming and decreasing of heavy metals levels in wastewaters [10]. There are several techniques used to assess heavy metals in environmental samples. These include flame and graphite furnace atomic absorption spectrometry (FGFAAS), CPE [11] neutron activation analysis, inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma mass spectrometry ICP-MS [12].

For the knowledge, this article is the first project worked in this WTP since founding it. The level of metals was assessed for both influent and effluent treatment process for one year.

This work aimed to assess: (i) the amount of heavy metals in urban waste water of *Saruhanli* district (ii) seasonal change of heavy metal concentration (iii) removal percentage of heavy metals from the WTP and finally the amount of heavy metals evacuated into Gediz River.

2. MATERIAL AND METHODS

In the present study, seasonal occurrence and concentration of all heavy metals (As, Se, Al, Ag, Sb, Ba, Hg, Cd, Pb, Mn, Cr, Fe and Ni) were investigated during the wastewater treatment process by ICP-MS. The study was conducted in the Saruhanli WTP of Manisa city located in Turkey's Aegean Region.

2.1. Describing of Sampling Site

Samples taken from each influent and effluent stage of *Saruhanli* WTP in Manisa Municipality which connected mainly to households Figure 1. Saruhanli WWTP founded in 2013 treating daily about 3000 m^3 of municipal wastewater and serving about 53.684 resident living in this district. The treatment process includes (i) mechanically primary solids removal followed by (ii) anaerobic treatment plant (iii) aerobic plant (iv)Primary sludge collecting (v) secondary sludge filtration by pumping (vi) exposure to UV disinfection finally the treated wastewater is discharged in Gediz river which is the second largest river in Anatolia, the final flowing into the Aegean Sea Figure 2.

Figure-1. Geographical map of study Place.

Source: www.turkiyerehberi.gen.tr.

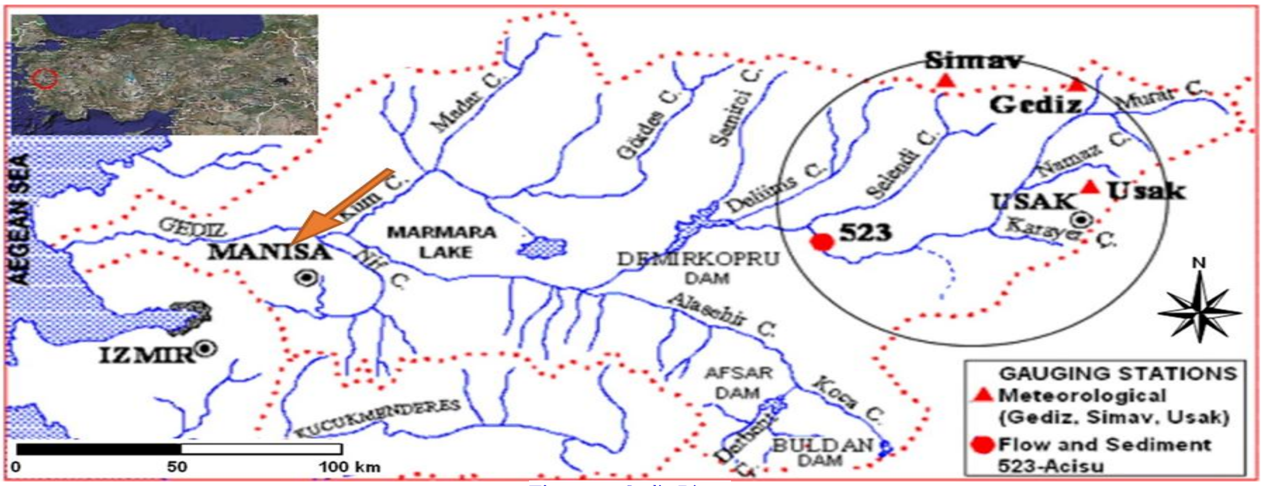

Figure-2. Gediz River.

Source: Ulke, et al. [13].

2.2. Sampling Method

Monthly sampling was taken from the Saruhanli WTP of Manisa city during the period from April 2018 to February 2019.

The water samples were measured according to APHA [14] one liter of wastewater by grape sample (5 cm deep from surface) from both influent and effluent part were taken by using clean bottles previously washed many times with ultra-distilled water, then samples were stored in the middle of a portable cool box and brought to the laboratory within maximum 8 hrs. Upon arrival at the laboratory, each sample was immediately processed.

2.3. Sample Preparation

Samples, were firstly centrifuged at 5000 rpm for 10 min. to separating particles into two part, Solid and liquid phase, both solid and liquid parts considered for total heavy metal concentration. The supernatant (liquid phases) filtered through 0.45 µm micro pore membrane filter to capture particulate matter and remove unwanted macro particles, Liquid phase treated with of 65% HNO_3. These samples were considered as dissolved phase of metals in wastewater sample, the precipitant considered solid phase, which utilized only for wastewater influent. Effluent samples already clear so examined directly without filtration. Solid phase was taken and treated with concentrated HNO_3 in microwave oven to digest metal associated molecules, then each phase analyzed separately by ICP-MS Agilent 7900. Heavy metal also prepared in same ICP-MS lab.

2.4. Removal Efficiency Calculation (RE %)

Removal efficiency of the heavy metals were calculated by using the equation [15]:

$$RE\ \% = (C_{inf} - C_{eff}) / C_{inf} \times 100\ \%$$

Where C_{inf} and C_{eff} are the concentrations determined in the influent and effluent wastewater, respectively.

3. RESULTS AND DISCUSSION

3.1. The Presence of Heavy Metals in Influent and Effluent

In this work 12 heavy metals (As, Se, Al, Ag, Sb, Ba, Hg, Cd, Pb, Mn, Cr, Fe and Ni) assessed during four seasons wastewater for both solid and liquid form. All these metals founded 100% in influent and about 90% for effluent parts (Total conc.) showed variations in concentrations except two metals (Al and As) removed completely for all season, similar results reported by Karvelas, et al. [16]. This result mean that Saruhanli treatment plants (WTPs) are completely efficient to control the discharge of both (Al and As) to the environment and need enhancement to remove other metals more efficiently.

3.2. Total Concentration of Heavy Metals for Influent

The result showed in Table 1 demonstrate the concentration of heavy metal for in both influent and effluent, all proposed heavy metals are presented 100% in influent with different concentration. The lowest concentration for all influent samples was Silver (Ag) and Pb which consider toxics for environment. The highest frequency in our work was Iron (Fe) similar to the result founded by Karvelas, et al. [16].

Because of these results belong to influent part, we cannot affirm the impact to the environment due to this part will be processed through treatment system but generally the concentration of heavy metals was high, therefore use different house hold products that rich with heavy metals which leaded to accumulation in influent, this reason also reported by Chipasa [17] and Chu, et al. [5].

3.3. Concentration of Heavy Metals in Solid Phase for Influent

In the sample preparation, explained above, we mentioned that the influent centrifuged into two phase to assess heavy metals in these two phase separately, the results are presented in Table 2, which demonstrate presence all metals also as founded in total concentration. in solid phase the concentration of heavy metals was much higher than in liquid phase which in the result increase the total concentration of heavy metal with compression if we assessed only liquid phase. The lowest concentration was (Ag, Hg, Cd, Sb and Ba) while the highest concentration was Iron (Fe) which similar the result of total concentration mentioned previously.

Table-1. Total concentration of heavy metal in four seasons.

Conc. / Metals	Concentration µg. L-1							
	Winter		Spring		Summer		Fall	
	I*	E*	I	E	I	E	I	E
Al	5342.366	0.000	5825.28	0.000	17182.607	<0.000	1944.349	<0.000
Cr	46.909	3.44	46.784	0.532	33.969	0.459	40.711	0.644
Mn	419.59	4.858	404.739	8.35	654.55	3.321	714.897	4.232
Fe	7833.129	46.338	8414.34	0.048	38151.867	2.68	10294.424	2.072
Ni	33.123	0.218	27.636	0.003	44.957	<0.000	31.992	<0.000
As	29.185	27.699	31.114	22.645	32.418	20.913	39.378	21.611
Se	5.618	1.132	4.539	0.96	5.005	0.417	6.493	0.42
Ag	0.152	0.000	0.15	<0.000	0.096	<0.000	0.319	<0.000
Cd	0.464	<0.008	0.322	0.044	0.444	0.021	0.19	0.029
Sb	0.795	0.573	0.532	0.51	0.868	0.763	1.296	0.832
Ba	285.683	107.129	274.431	52.594	229.24	60.92	426.658	81.84
Hg	0.342	0.027	0.289	0.021	0.801	0.016	0.626	0.017
Pb	14.909	0.135	12.777	0.33	15.748	0.533	3.717	0.485

Table-2. Solid part concentration of heavy metals in four seasons.

Metal	Concentration µg. L-1			
	Winter	Spring	Summer	Fall
Al	5307.546	5825.28	17178.069	1939.699
Cr	41.109	44.478	31.19	37.876
Mn	318.69	329.756	626.004	686.745
Fe	7084.339	8379.503	38061.038	10208.876
Ni	26.303	24.231	40.651	26.325
As	13.844	12.04	8.604	18.882
Se	2.958	3.215	3.445	3.704
Ag	0.152	0.141	0.094	0.319
Cd	0.319	0.297	0.404	0.177
Sb	0.043	0.306	0.255	0.83
Ba	172.288	194.727	141.873	333.931
Hg	0.162	0.262	0.081	0.2
Pb	10.994	12.549	15.168	3.239

3.4. Concentration of Heavy Metals in Effluent

The presence and concentration of heavy metals in this part consider very critical because of the whole amount of metal will discharged into environment without utilizing extra treatment way and finally lead to eco-toxicity. In the effluent wastewater only liquid phase examined due solid particles was very low so the sample assessed directly without filtration, the results in Table 1. show the concentration of heavy metals during four season, the highest metal content was Fe and the lowest was Hg, Karvelas, et al. [16] reported that the highest level was for Mn 77% and the lowest was for Fe 37%.

The treatment results showed ideal removing of Aluminum which assessed as zero amount and this fit with WHO 2017 and EPA 2018 water standards, other metal results were very high, such as Parvin, et al. [8] mentioned in his paper that the US Environmental Protection Agency (EPA) has adopted an arsenic maximum contaminant level of 10 µg. L^{-1}. this mean that despite treatment processes but still in high level which impact on water environment causing (death of aquatic life, algal blooms, habitat destruction from sedimentation, debris) especially water environment of Gediz river because the effluent discharged in it and with continuous of this operation lead to Aegean Sea impact by the heavy metal high content effluent stream, Irrigation with this effluent also impact soil and plants this problem also reported by Houari, et al. [18].

3.5. Heavy Metals Removal Percentage during Seasons

The amount removed heavy metals from influent and that passed to the effluent considered for removal percentage, this result very important because it reveal the quality of wastewater treatment plant system for processing of the waste and resulting a few amounts of heavy metals in effluent part before discharging, whenever the removal percentage was high its mean that the amount of removed heavy metal is high and vice versa.

For this work the highest removal was with Al and Ag , both of them was 100% and this reveal that the quality of WTP is high for removing these metals showed in Figure 3.

Houari, et al. [18] reported that the removal percentage for Cd(II), Ni(II), Pb(II) and Cu(II) ions were more than 97%, this results was similar to the percentage of WTP in our work.

Yuan, et al. [19] reported that the removal of Pb and Cd reached 89.1% and 99.3% respectively, the result of Pb was lower than our results but the result of Cd was higher than our results.

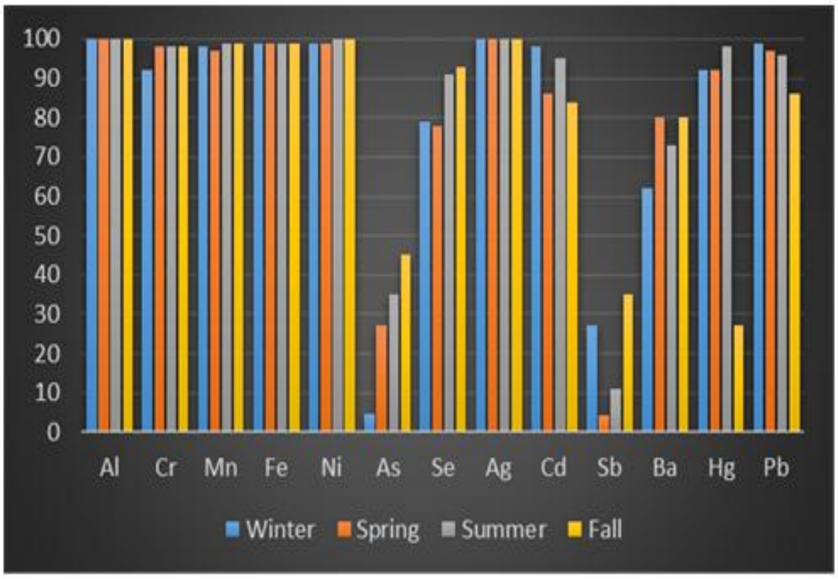

Figure-3. Seasonal percentage of heavy metals removing.

The yearly removing average was ranged between 96% to 100 % for (Al, Cr, Mn, Fe and Ni), these was the highest removing yearly average. While Ag, Sb and As processed as the lowest yearly removing average ranged between 11%, 19.35% and 27.87 % prospectively, other metals were in medium averages as showed in Figure 4.

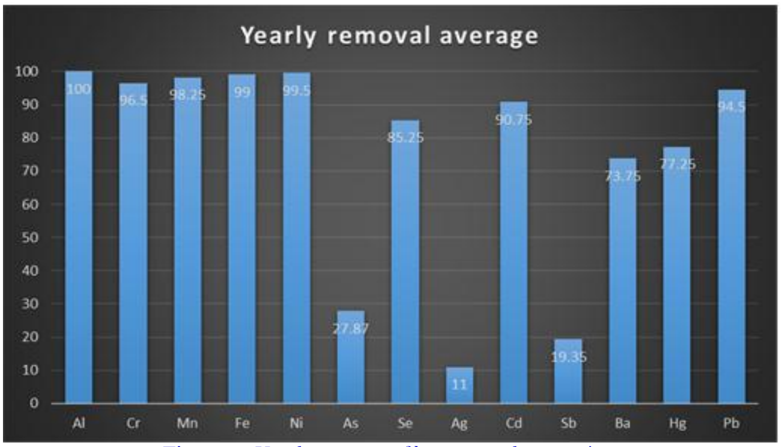

Figure-4. Yearly average of heavy metals removing.

Comparison with other researches we found wide ranges of removing with different results according to the methods used for processing of wastewater. Such as, Yang, et al. [20] they used Chitosan Electrospun Nanofiber membranes for heavy-metal removal and the results was high percentage of removing during short time of processing while the WTP in our work did not use this technique which decrease the amount of heavy metals more in the effluent wastewater.

Ye, et al. [21] they designed unique method to increase the removal rate by using nano filtration membranes consisting of quaternized polyelectrolyte complex nanoparticles, the technique summarized by using Polyelectrolyte Complex Nanoparticles (PEC NPs) with tunable quaternary ammonium groups to prepare quaternized polyelectrolyte complex membranes (QPECMs) for Nano filtration process via surface coating and glutaraldehyde cross linking method which lead to increase in both water permeability and enhanced ion selectivity of metal cations finally lead to increasing the percentage of heavy metals removal. Other techniques also can be used as removing solutions as explained in our previous article [22].

4. CONCLOUSIONS

The presence, concentration and removal percentage of thirteen heavy metal (As, Se, Al, Ag, Sb, Ba, Hg, Cd, Pb, Mn, Cr, Fe and Ni) assessed by using ICP-MS in both influent and effluent steps of *Saruhanli* wastewater treatment plant of *Manisa* city, western Turkey.

According to work results we concluded:

- All mentioned metals was presented in influent and effluent except (Al and As) removed completely.
- The concentration of metals in solid part was higher than liquid part of influent.
- The highest yearly removal average after (Al and Ni) was for (Fe, Mn and Cr) while the lowest removal average was for (Ag, Sb and As) and this consider critical number for water environment.
- The WTP need renew treatment technologies like Nanotubes, highly Adsorption technique to capture more amount of metal before discharging.
- The high concentration of metals in effluent wastewater means that using multiple household requirements containing high amounts of these metals. So, as well as wastewater treatments also should be there continuous investigation on the metal contents of used material in houses.

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