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Article

Examination of Heavy Metal Concentration in Wastewater in and around Chittoor District, Andhra Pradesh

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ABSTRACT

The investigation aims to determine the concentration level of heavy metals (HMs) in industrial wastewater in Chittoor district. The existence contamination of HM causes a serious problem around the universe due to the several sources, toxicity, accumulative behavior, and non-biodegradable property of HMs. The HMs contamination in industrial wastewater around Chittoor district is prominent. Some parameters such as pH, hardness, and electrical conductance are used to analyze for each metal. A simple hot plate digestion procedure was employed using acids (HNO_3, Hcl) and developed to determine the concentration of these metals lead (Pb), iron (Fe), cadmium (Cd), nickel (Ni), and chromium (Cr) in water by atomic absorption spectrometry technique. This shows that the presence of Ni, Fe, Cr, Cd, and Pb in the study area has a significant influence to health. Especially, Cd, Cr, Fe, and Pb exhibited high significance toxicity effect even at lower concentration levels of HMs which obtained was usually higher than the permissible limit for the safe environment as prescribed by the World Health Organization and Indian standards. The study region point out the health risk due to wastewater for residents and aquatic system which shows an ultimate concern for their survival in the region.

Key words: Industrial wastewater, Heavy metals, Parameters, Atomic absorption spectrometry.

1.INTRODUCTION

Water is a resource of prime importance. Water is essential for the very existence of life on the globe. Water pollution has become a continuous increasing problem on the earth which is affecting the human and animal lives in all aspects. Water pollution is the contamination of drinking water by the poisonous pollutants generated by the human activities. They are polluted through many sources such as urban runoff, agricultural, industrial, sedimentary, leeching from landfills, animal wastes, and other human activities. All the pollutants are very harmful to the environment. Human population is increasing day by day and thus their needs and competition leading pollution to the top level. We need to follow some drastic changes in our habits to save the earth water as well as continue the possibility of life here. Water pollution through industry is easily the most widespread type of water pollution in all countries around the world, too.

Nowadays, the society is concerned regarding the outcome of heavy metal (HM) ions in the surrounding environment. The tremendous increase in the use of HMs over the past few decades has inevitably resulted in an increased flux of metallic substance in the aquatic environment. Industrial wastewater contains a higher amount of HMs that can pollute the water when it is discharged to the nature. Toxic HMs of particular concern in the treatment of industrial wastewaters include zinc, copper, nickel (Ni), mercury, cadmium (Cd), lead (Pb), and chromium (Cr). HMs are the elements that have >5 times the specific gravity than that of water. HMs are one of the most toxic types of water pollutants. At least 20 metals are considered to be toxic and approximately half of these metals are emitted to the environment in quantities that are risky to the surroundings, additionally to the human health.

Wastewater containing HMs originated mainly from metal plating facilities, mining operations, fertilizer industries, tanneries, batteries, paper industries and pesticides galvanizing plants, stabilizers, thermoplastics, pigment manufacture, etc. [1].

These industries discharge HMs and wastewater directly or indirectly into the environment in all countries. Due to their toxicity and non-biodegradability, they tend to accumulate in a living organism. Therefore, they cause numerous diseases and disorders. Of the 92 naturally occurring elements, approximately 30 metals and metalloids are potentially toxic to humans, Be, B, Li, Al, Ti, V, Cr, Mn, Co, Ni, Cu, As, Se, Sr, Mo, Pd, Ag, Cd, Sn, Sb, Te, Cs, Ba, W, Pt, Au, Hg, Pb, and Bi. HMs are the generic term for metallic elements having an atomic weight higher than 40.04 (the atomic mass of Ca) [2]. Although some individuals are primarily exposed to these contaminants in the workplace, for most people, the main route of exposure to these toxic elements is through the diet (food and water). The contamination chain of HMs almost always follows a cyclic order: Industry, atmosphere, soil, water, foods, and human. Although toxicity and the resulting threat to human health of any contaminant are, of course, a function of concentration, it is well-known that chronic exposure to HMs and metalloids at relatively low levels can cause adverse effects [3-7].

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The liquid-wastewater is essentially in industrial effluent and the water thrown out by the community after it has been used in a variety of applications. In recent years, HMs, besides other pollutants, have increased to reach dangerous levels for the living environment in many regions. The presence of toxic and polluting HMs in wastewaters from industrial effluents, water supplies, and mine waters, and their removal has received much attention in recent years. The amount of HMs that industrial wastewaters often contain is considerable and would endanger public health and the environment if discharged without adequate treatment.

In light of the facts, treatment of HMs containing industrial effluent becomes quite necessary before being discharged into the environment. The scientists and environmental engineers are, therefore, facing a tough task of cost-effective treatment of wastewater containing HMs. Industrial wastewater contains HMs such as arsenic, Cd, Cr, copper, Pb, mercury, and Ni which are very toxic and carcinogenic in nature [8]. Indiscriminate discharge of industrial effluents into the environment is leading to the contamination of water bodies including groundwater. Contamination of groundwater resources Pb to a serious groundwater pollution problem [9].

Although techniques such as inductively coupled plasma optical emission spectrometry (ICP-OES) and ICP-mass spectrometry (MS) have gained popularity for measuring minerals in water. Atomic absorption spectrometry (AAS) is still extensively used, as it is a simple, inexpensive and rapid method for water quality. The most widely applied separation and detection techniques for quantification of these elements in biological and environmental samples are included, a variety of inorganic techniques can be used to measure heavy elements in wastewater including AAS, graphite furnace (or electrothermal) AAS, ICP-OES, and ICP-MS. Depending on the number of elements to be determined, the expected concentration range of analyzes and the number of samples to be run, the most suitable technique for business requirements can be chosen as they provide valuable toxicological data for hazard and risk assessments. Even though the about techniques gained the popularity for measuring the several other metal ion analysis techniques for wastewater samples, the AAS method is still extensively used due to the reproducibility of results, simple, short analysis time, cost-effective, lower level detection, hyphenated in nature, and rapid method for water quality. Therefore, we have attempted to describe the atomic absorption spectroscopic analytical technique in a simple manner. In this context, HMs such as Pb, Iron (Fe), Cd, Ni, and Cr have been studied, and the concentration levels of each HMs are determined in water using AAS technique. The pH of the wastewater may affect the quality of the water by increasing the toxicity of the metal as the pH decreases, electrical conductance, and hardness also measured for the HMs. The schematic depiction to obtain the concentration of HMs by AAs is shown in Figure 1.

2. EXPERIMENTAL

2.1. Sample Spot Location

In the present study, five industrial areas were selected for the collection of samples as listed in Table 1 which was located in and around Chittoor district, as marked in the map as mentioned in Figure 2.

Tirupati is one of the most famous pilgrim sites, which was developed and having polluted industrial area in Chittoor district. The sampling area is located between 12.37 and 14.8 northern latitudes and 78.3 and 79.55 eastern longitudes, as shown in the given map below. The geographical area is 1515100 hectares of land consisting of big and small-scale industries such as pharmaceutical units, engineering units, steel processing industries, battery industries, chemical units, textile industries, and paints.

The effluent water from these industrial zones is incessantly disposed of into the soil and later accumulates into plants. The population in these regions is underneath risk of ecological contamination.

2.2. Reagents and Chemicals

All chemicals and reagents used were of high purity analytical grade (analytical reagent grade). HCl (37%), HNO_3 (69–72%), and

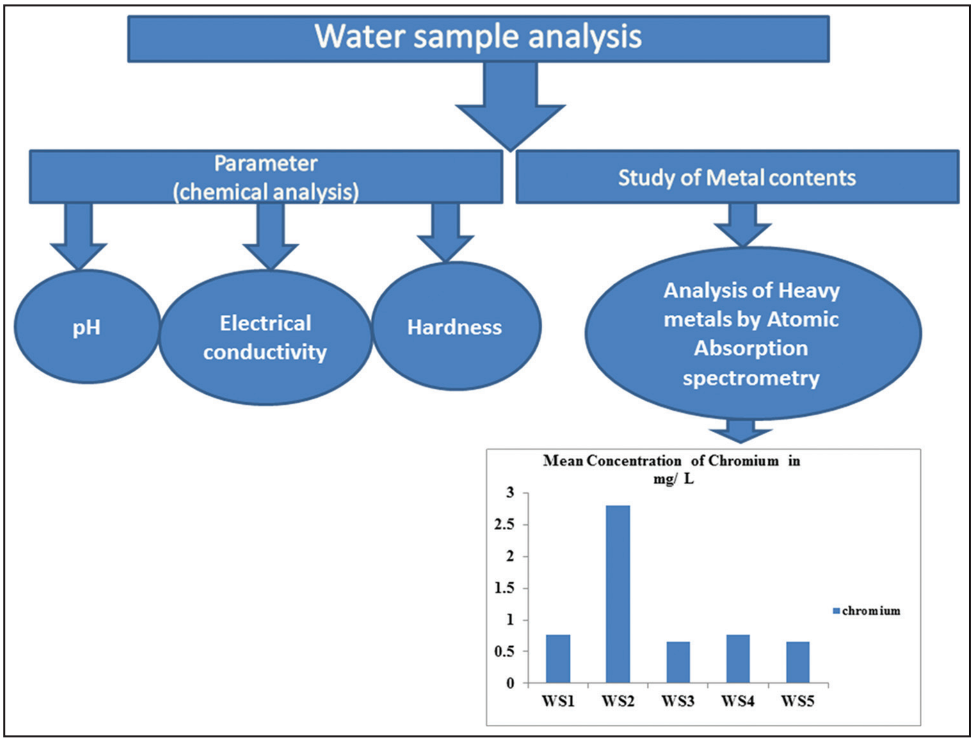

Figure 1: Schematic depiction to obtain the concentration of heavy metals by atomic absorption spectrometry.

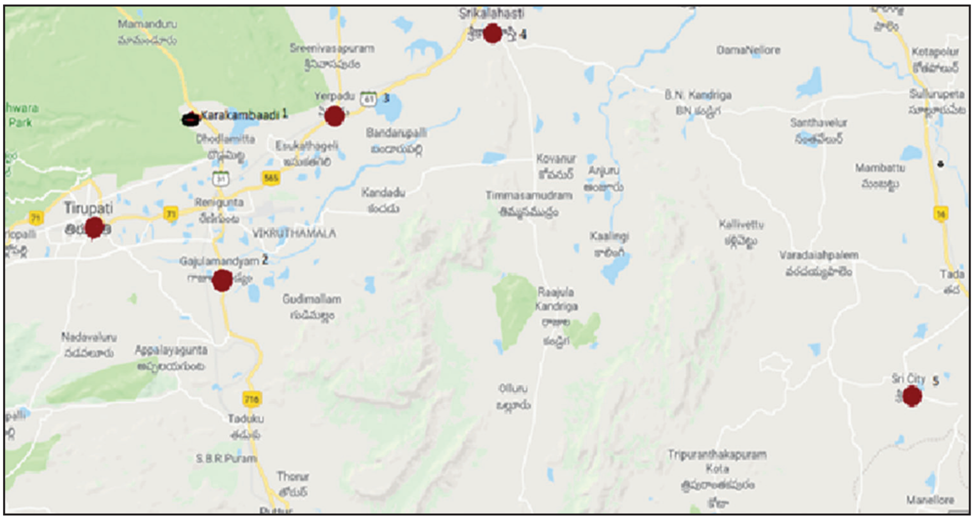

Figure 2: Pointing the sample spot locations

Table 1: Industrial wastewater sampling location in and around Chittoor district.

Water sampling number	Location of sampling
WS1	Karakambadi
WS2	Gajjulamandyam
WS3	Yerupadu
WS4	Srikalahasti
WS5	Sricity

WS: Water samples, WS1: Karakambadi industrial area, WS2: Gajjulamandyam, WS3: Yerpedu industrial area, WS4: Srikalahasti, WS5: Sricity.

H_2SO_4 (98%) were used to digest the samples while corresponding metal salts are Mohr's salt (Fe) (99%), Pb $(NO_3)_2$ (99.5%), $CdCl_2.H_2O$ (99.99%), Cr $(NO_3)_2$ (99.99%), and $NiCl_2.6H_2O$ (99%) were used as metal standards [10]. Calibration standards of each metal were prepared by appropriate dilution of a stock solution of 1000 ppm. Mill-Q water was used for making the standard solution, rinsing glassware, and washing sample bottle.

2.3. Collection of samples and preparation

A 2 L capacity polythene bottles were used for collection of wastewater samples. These polythene cans were washed first with tap water, soaked in nitric acid solution overnight to remove any impurities, and then washed with Milli-Q water. Finally, at the time of sampling, the polythene bottles were rinsed with the sample water, recapped, and labeled before collection of samples. Five different industrial samples were collected from different locations in and around Chittoor district. The samples were acidified with 10% nitric acid stored and were later conveyed to the laboratory for analysis. The addition of acid to the water sample is to keep the metal ions in the dissolved state, as well as to prevent microbial activities [7]. Preliminary digestion of water sample was necessary to release the metals associated with suspended as well as colloidal organic matters. The samples were first acidified with concentrated HCl to adjust the pH to the value by 2, and concentrated HNO_3 was added to each 50 ml acidified sample and allowed to evaporate slowly in a hot plate, reducing the volume to about 15–20 ml. All the samples were analyzed within 2 days after sample collection to eliminate or minimize not only precipitation of analyzes but also any possible contaminations. The digested samples were allowed to cool to room temperature. They were then filtered through Whatman's 0.45 µm filter paper and the final volume was adjusted to 50 ml with Mill Q-water and stored. Our studies focused on these metals Fe, Cd, Pb, Cr, and Ni.

2.4. Preparation of Standard Solutions for AAs

Standard solutions of metals (1000 ppm) were prepared from either the metal or soluble salt of the metal of highest purity (analytical grade reagent available). Metals were dissolved in acid HNO3 and made up to 1 L in a volumetric flask. Different concentrations 2 ppm, 4 ppm, 6 ppm, and 8 ppm were prepared from this stock solution for plotting calibration graph for AAS analysis [11].

2.5. Physicochemical Analysis of Samples

The HMs level in water depends on the physicochemical parameters of water here we have focused on pH, conductivity, and hardness.

3. HMS ANALYSIS BY AAS TECHNIQUE

This paper proposes an analytical procedure for the determination of HMs in the environmental sample, i.e., industrial wastewater by AAS. The standard operating parameters with wavelength were set and given in Table 2. During analysis, the air-acetylene is used, and hollow cathode lamps for HMs (Shimadzu-6300) were used as a radiation source.

4. RESULTS AND DISCUSSION

The results of the physicochemical analysis of different wastewater samples are listed in Table 3. Physical parameters include temperature and color of water while chemical parameters include pH, dissolved oxygen contents, alkalinity, hardness, and electrical conductivity. The parameters used in the present work are as electrical conductivity, pH, and hardness were measured. Table 3 shows the results for pH, electrical conductivity, and hardness of collected samples. The World Health Organization (WHO) normal ranges for pH are 6.5–8.5 and the pH of all the collected samples was recorded within the normal range. The WHO normal range for electrical conductivity of water is 400–600 µS/cm. In all the analyzed samples, the electrical conductivity is exceeding the WHO permissible limit range. The WHO normal range for the hardness of water is 50–250 mg/L, but the values show above the limit values [12].

The analysis was carried out on wastewater at several locations in Chittoor district to determine the concentration of five HMs (Fe, Pb, Cr, Cd, and Ni). The concentration of each metal was detected and

Table 2: Wavelengths used for determination of different HMs.

Metal	Wavelength (nm)
Fe	248.3
Ni	232.00
Cr	357.87
Cd	228.80
Pb	283.31

HMs: Heavy metals, Fe: Iron, Ni: Nickel, Cr: Chromium, Cd: Cadmium, Pb: Lead.

Table 3: Physiochemical parameters of water.

Water sample number	Conductivity (µS/cm)	pH	Hardness (ppm)
WS1	1165	7.84	280
WS2	1214	8.15	310
WS3	1315	7.79	270
WS 4	1487	8.28	290
WS 5	1171	8.20	311

Table 4: Concentration of metal ions in water samples (mg/L).

Water samples	Iron	Cadmium	Lead	chromium	Nickel
WS1	1.12	1.16	1.7	0.76	2.24
WS2	21.2	0.085	0.9	2.8	1.95
WS3	1.28	0.077	0.23	0.65	1.65
WS4	1.21	0.078	0.1	0.76	0.98
WS5	1.36	0.076	1.07	0.65	0.14

WS: Water samples, WS1: Karakambadi industrial area, WS2: Gajjulamandyam, WS3: Yerpedu industrial area, WS4: Srikalahasti, WS5: Sricity.

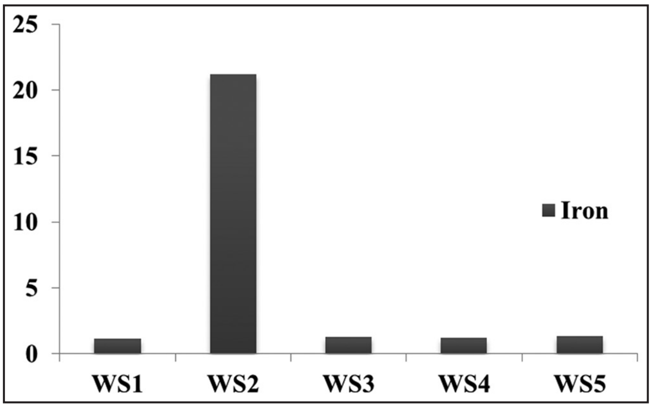

Figure 3: Concentration of metal ions in water samples (mg/L) (WS: Water samples): WS1: Karakambadi industrial area, WS2: Gajjulamandyam, WS3: Yerpedu industrial area, WS4: Srikalahasti, WS5: Sricity.

tabulated in Table 1. For the protection of human health, guidelines for the presence of HMs in water have been set by different International Organizations such as United States Environmental Protection Agency, World Health Organization (WHO), and the European Union

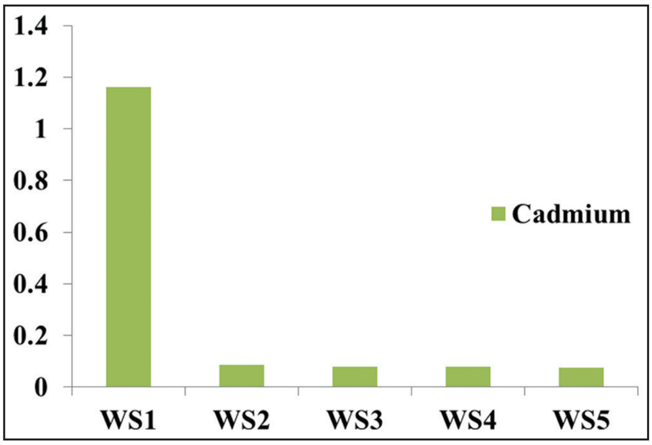

Figure 4: Concentration of metal ions in water samples (mg/L) (WS: Water samples): WS1: Karakambadi industrial area, WS2: Gajjulamandyam, WS3: Yerpedu industrial area, WS4: Srikalahasti, WS5: Sricity.

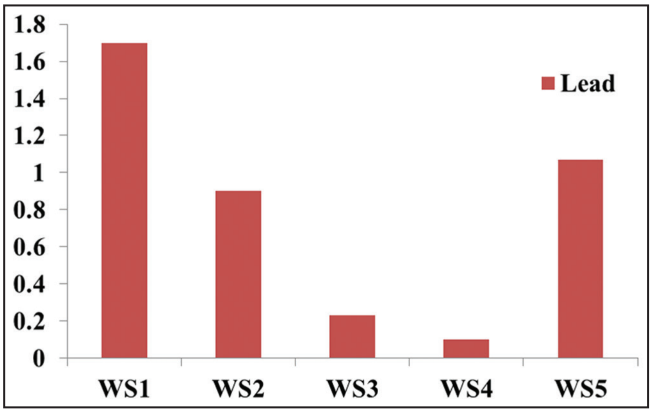

Figure 5: Concentration of metal ions in water samples (mg/L) (WS: Water samples): WS1: Karakambadi industrial area, WS2: Gajjulamandyam, WS3: Yerpedu industrial area, WS4: Srikalahasti, WS5: Sricity.

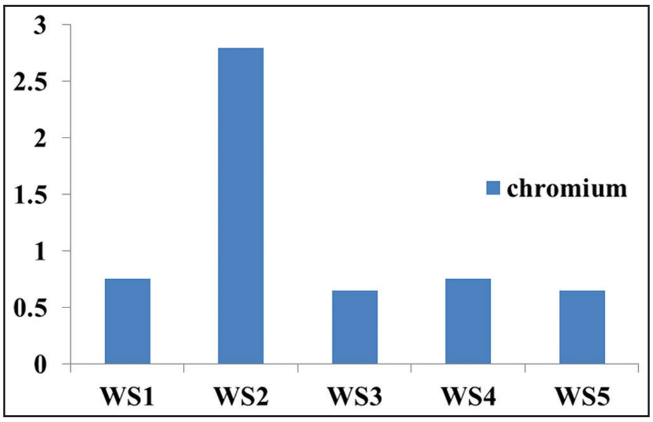

Figure 6: Concentration of metal ions in water samples (mg/L) (WS: Water samples): WS1: Karakambadi industrial area, WS2: Gajjulamandyam, WS3: Yerpedu industrial area, WS4: Srikalahasti, WS5: Sricity.

Commission [13]. Thus, HMs have permissible limits in water as specified by these organizations. The concentrations of HMs in five industrial areas are mention in Table 4.

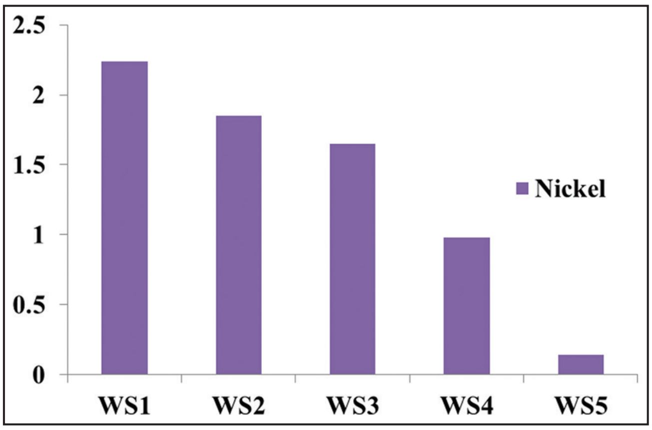

Figure 7: Concentration of metal ions in water samples (mg/L) (WS: Water samples): WS1: Karakambadi industrial area, WS2: Gajjulamandyam, WS3: Yerpedu industrial area, WS4: Srikalahasti, WS5: Sricity.

4.1. Fe

The concentration of Fe in the samples for the different location was given in Figure 3. The Fe concentration in the WS2 sample was showing peak value, i.e., 21.2 mg/L and the lowest value in the remaining samples, i.e., in between 1.12 and 1.36. The Fe concentrations in the sample WS2 have exceeded the WHO standards limit. The permissible set value for Fe in water is 0.1 mg/L, >0.3 mg/L can damage paper, spoil fabric corrode the internal walls of boilers, and also impart the taste of water. As well as, it promotes the increase of Fe bacteria and quick processing of rust takes place for all ferrous metals that are closer in contact with the water [14-16].

4.2. Cd

Figure 4 represents the Cd concentration in the samples for a different location. Based on Figure 4, the Cd concentration in the WS1 sample was showing greater value, i.e., 1.16 mg/L and the lowest value in the remaining samples, i.e., in between 0.076 and 0.085. The Cd concentrations in the sample WS1 have exceeded the WHO standards limit. The permissible set value for Cd in water is 0.1 mg/L. Greater than this limit causes cancer, lungs insufficient disturbances in liver, and kidney damages to the living system.

4.3. Pb

Absorption of Pb is high in the WS1 sample, i.e., 1.7 mg/L as shown in Figure 5 and ultimately lower in the samples WS4 and WS5 region, i.e., 0.01 and 0.04 mg/L. However, the observed concentration levels of Pb in the study area are higher than the WHO permissible limits. The sources of the Pb are from the Battery manufacturer, metal plating, textile, automotive and petroleum industries [17], and their toxic effects, causes damage to the live hoods.

4.4. Cr

The maximum contamination level standard value for Cr is 0.05 mg/L, and maximum acceptable limit as per the WHO is 0.05 mg/L [18]. The Cr values in the entire water samples range between 0.65 mg/l and 2.80 mg/l. The concentration values are above the maximum tolerable level of Indian standards. The maximum concentration of Cr was observed in the WS2 sample, i.e., 2.80 mg/L ultimately the lowest concentration is seen in the remaining samples, i.e., from 0.65 mg/L to 0.76 mg/L as exposed in Figure 6.

4.5. Ni

The concentration of Ni in the sample for various locations was given in Figure 7. Based on Figure 7, the Ni concentration was highest in sample WS1, i.e., 2.24 mg/L and the lowest is seen in the region WS5 0.14 mg/L. The values were compared with the WHO standards which were above the maximum tolerable level and the limit value for Ni is 0.20 mg/L. Excess limit gives rise to the cancers, asthma, carcinogenesis, allergic contact, dermatitis, oral hypersensitivity, and reproductive toxicity [19].

5. CONCLUSION

Developed industrialization has tremendously added toxic pollutants to the environment. The most abundant pollutants in the wastewater are metals such as Pb, Cr, Ni, Cd, As, and Cu. This study focused on industrial zones, in and around Chittoor district which has different types of industries. The researchers attempted to evaluate the potential of HMs contamination in industrial effluents using AAS which was used widely and applicable. These AAS is useful not only for metal ion analysis in environmental samples but also for the speciation studies of metals in environmental samples. As we have seen, the concentration levels of metals depend on the sampling location. In the present work, the HMs such as Fe, Cd, Pb, Cr, and Ni are showing the concentration levels, above the permissible limit which were set by the Indian Standards. The result shows that pH of all the water samples was within the permissible limits, whereas the values of electrical of all the collected samples were found to be extremely higher than permissible limits set by the WHO. Similarly, hardness was also records to be higher than the WHO permissible limits. In general, the result shows that the concentrations of certain elements are higher in the samples. Hence, the study concluded that the industrial wastewater is enriched with HMs to a concentration that shows the potential environmental and health risks in the long term.

6. ACKNOWLEDGMENT

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