Analysis of Copper from Electroplating Industry Waste Water and Its Reuse as Fungicide

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Abstract: ***Effluent from electroplating industry involved in copper plating and other metal polishing work contain various heavy metal(Cu, Fe, Ni, Pb, Mn and Zn) which have severe adverse effect on health . The present work analyzes heavy metal present in plating shops for a period of one year. Highest copper metal concentration (27.60mg/L) was observed during post monsoon at site AB-5, least copper metal concentration (0.23 mg/L) was observed for during monsoon at site AB-2. The waste water was monitored for other parameters (BOD, COD, Alkalinity, Acidity, pH and conductivity) which give quality index of the waste water let off from these industries. After monitoring of the waste water, copper diethyldithiocarbamate fungicide was synthesized under lab condition by precipitation and its solution within pH range of 9-9.2 was prepared. Its effectivity for the cure of fungal disease of potato, tomato, okra, brinjal, sunflower and rose has been studied. Early blight of tomato and potato, Buckeye rot of tomato and leaf spot of sunflower has been successfully cured by copper diethyldithiocarbamate synthesized. Our research paper aims to draw attention towards analysis and removal of copper metal from the waste water discharged from five electroplating units in Agra and recycle of the metal in to its diethyldithiocarbamate fungicide and prove the application of copper diethyldithiocarbamate fungicide in control of fungal disease of potato, tomato and sunflower which have great export and market value.***

Keywords : ***diethyldithiocarbamate, BOD, COD, Alkalinity, Acidity***

Introduction:

Industrialization and urbanization have led to discharge of industrial effluents, which in turn pollute the ecosystem. The disposal of effluents has become a serious techno-economic problem particularly due to rising cost of disposal and growing awareness of pollution hazards. Out of all waste water discharges effluents from industries such as electroplating, oils, and paints, textiles etc pose a threat as these waste water is usually dumped in to natural water resources like rivers, lakes, ponds etc and makes the same unfit for human, animal, plant consumption as well as for industrial use [(1)]. The metal finishing processes often involve cleaning, conversion coating, organic coating, plating, anodizing, coloring and case hardening. The cleaning process often uses acid pickling to prepare the metal plating.

The major constituents in the waste water being generated from the metal finishing processes are cyanides, various metal ions [Fe, Cu, Ni, Ag, Mn, Pb, Zn and Cr (VI)] oils , greases, organic solvents, acids and alkalies. The characteristics of the waste stream from electroplating industries are so toxic and corrosive due to the presence of these metals [Fe, Cu, Ni, Ag, Mn, Pb, Zn and Cr (VI)] which are termed as heavy metals [(2, 3, 4)].

Metals can be introduced in to aquatic system through effluent discharges from various industrial operations including mining, chemical manufacture and electroplating[(5)] and their increased concentration in aqueous environment is capable of causing phytoxicity, bioconcentration and biomagnifications by organisms[(6)]. Heavy metals become toxic when they are not metabolized by the body and accumulate in the soft tissues.

Among industrial sources, the main contributors of copper are metal pickling baths, copper plating baths, waste waters from the metal work and foundries, mine water, mine tailing ponds and acid mine drainage from lead mining [(7, 8, 9)]. Copper concentration causes diarrhoea, sporadic fever, hypertension, hemoglobinuria, hematuria, uremia, coma and cancer suspected. Copper also produces pathological changes in brain tissue. Heavy metals from waste water can be removed by using membrane technology coupled with other treatment process[(10)] and can be recycled by precipitating metals (Cu, Fe, Mn, Ni, Pb and Zn) present in electroplating waste water with sodium diethyldithiocarbamate and thus in the process forming respective metal diethyldithiocarbamte which works as fungicide in controlling diseases of vegetables and ornamentals[(11)]. The carbamate fungicides are all derivatives of dithiocarbamic acid. These fungicides are widely used and have low toxicity[(12)].Main work of the present study comprises of reuse of copper metal present in waste water of electroplating industry, by preparing copper diethyldithiocarbamate fungicide under lab condition and testing its efficacy in fungal disease management of vegetable and ornamentals.

Material and Method:

Waste water from five electroplating sites AB-1, AB-2, AB-3, AB-4 and AB-5 of Agra city were assessed for copper metal concentration and other physic-chemical parameters (pH, Conductivity, BOD & COD). pH was measured within two hours from collection on laboratory arrival with the help of pH meter after calibration of the instrument and conductivity by digital conductometer. BOD(Biological oxygen demand) and COD (Chemical oxygen demand) were determined by titration method.

Copper metal analysis was performed on an Atomic Absorption Spectrophotometer (Perkin –Elmer A.Analyst 100) following the condition of operation of the instrument.

Atomic Absorption Spectrophotometer uses acetylene and air as fuel and oxidant respectively. The standard solution of copper metal was made using analytical grade reagents for calibration purpose. Samples of each site were filtered and digested with nitric acid before metal concentration analysis and wave length for copper metal detection used is 324.8nm. Synthesis of Copper diethyldithiocarbamate powder and its solution for spraying on vegetables and flowers was done in the laboratory. For this copper diethyldithiocarbamate powder was prepared by mixing 0.1 M solution of copper carbonate and sodium diethyldithiocarbamate. Precipitate of copper diethyldithiocarbamate was obtained which was filtered and washed with double distilled water and dried in oven at a temperature of 125^0C. 0.01M solution of copper diethyldithiocarbamate was prepared in a mixture of ethyl alcohol and water in the ratio of 7:3 V/V with a pH range of 9-9.2. Spraying test was conducted in the study field area in which there were two rows. Each row has potato, tomato, brinjal, rose and sunflower plant. First row was not subjected to any spraying treatment where as second row was subjected to copper diethyldithiocarbamate spraying and spraying was repeated after fourteen days in dry season to avoid washing away. Results are reported from study conducted for effectivity check of copper diethyldithiocarbamate in the study field as well as application on some randomly found diseased plants other than the study area.

Result and Discussion:

Physico-chemical characteristics pH, conductivity, BOD, COD (Table & Graph :3, 4,5 and 6) and copper metal concentration(Table & Graph: 2) from various electroplating sites in three seasons- premonsoon, monsoon and post monsoon were recorded. In Premonsoon season highest pH was observed in site AB-2, value ranging to 7.76, conductivity value was found to be highest in site AB-5, Biological oxygen demand (BOD) which is organic pollution indicator and is the rate of removal of oxygen by microorganisms in aerobic degradation of dissolved or even particulate organic matter in water was highest in AB-1, tolerance limit of BOD for industrial effluents discharged in to inland surface waters (IS:2490-1974) is 30 mg/L(Table 1: IS:2490-1974) and BOD values were above this prescribed limit during all seasons. Chemical oxygen demand (COD) which is the measure of oxygen required in oxidizing organic compounds present in water by means of chemical reactions has tolerance limit of 250 mg/L(Table 1: IS:2490-1974) for discharge of industrial effluents in to inland surface waters was highest in site AB-5 (270 mg/L) during premonsoon season.

Similarly site having highest pH, conductivity, BOD and COD values during monsoon and post monsoon season respectively were AB-4, AB-1 for pH, AB-4, AB-5 for conductance, AB-3, AB-2 for BOD and AB-4 and AB-5 for COD value.

Copper which is industrial health hazard and excess of which in human body causes hypertension, sporadic fever, uremia, coma and even death was found highest in site AB-2 during premonsoon and in site AB-5 during monsoon and post monsoon. Site AB-1 was least metal polluted during all three seasons of a year. Tolerance limit for copper concentration in industrial effluents discharged in to inland surface water is 3 mg/L and during post monsoon season waste water from site AB-4(3.68 mg/L) and AB-5(27.60mg/L) crossed this prescribed limit. Copper diethyldithiocarbamate 0.01M solution prepared in laboratory was found effective in curing potato plant infected by alternaria solani fungi which caused initial symptoms of early blight disease such as Dark, dry, small spots on the leaves which grow to become brown-black, circular to oval areas. Spots have target appearance, caused by concentric rings of raised and depressed dead tissue. Similar effecticveness of Copper diethyldithiocarbamate was found in case of tomato plants infected by fungi Alternaria Solani and Phytophthora parasitica which caused early blight and Buckeye rot disease characterized by symptoms such as Small, black lesions mostly on the older foliage. Tissue surrounding the spots turn yellow and in case of buckeye rot symptoms such as Brownish spots at point of contact between the fruit and the soil. Concentric rings on enlargement of spots appear. Copper diethyldithiocarbamate spraying on sunflower plant infected by fungus Alternaria helianthi, causing the leaf spot disease of sunflower showed positive impact in the cure of disease.

Conclusions:

It is thus concluded that quality of waste water discharged from electroplating industry need to be treated before their discharge in to open drains as these effluents are highly corrosive and toxic and their discharge directly in to rivers. (Yamuna river in present study) result in mass mortality of aquatic culture. Standards of discharged effluents in to inland surface water has to be maintained by stringent rules and policies. Presence of heavy metal such as copper in present case shows that such harmful metal can be recovered from waste stream by reverse osmosis and nano filtration and can be successfully recycled in to their diethyl dithiocarbamate fungicide and effectively can be used in curing fungal disease of vegetables and flowers. Copper diethyldithiocarbamate prepared in laboratory successfully cured early blight disease of potato and tomato, buckeye rot disease of tomato and leaf spot in sunflower plant. The study is effective two way- in metal pollution prevention and in resource conservation. The Copper diethyldithiocarbamate is contact fungicides have multisite activity and thus is active against more than one point in metabolic pathway in a pathogen and can work against more than one critical enzyme needed by the fungus for its growth. According to FRAC (Fungicide resistance action committee) since diethyldihiocarbamates are contact and multisite in activity they have low risk to resistance development problem.

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IJSET
International Journal of Scientific Engineering and Technology (ISSN : 2277-1581)
Volume No.3, Issue No.1 pp : 43-46 1 Jan 2014

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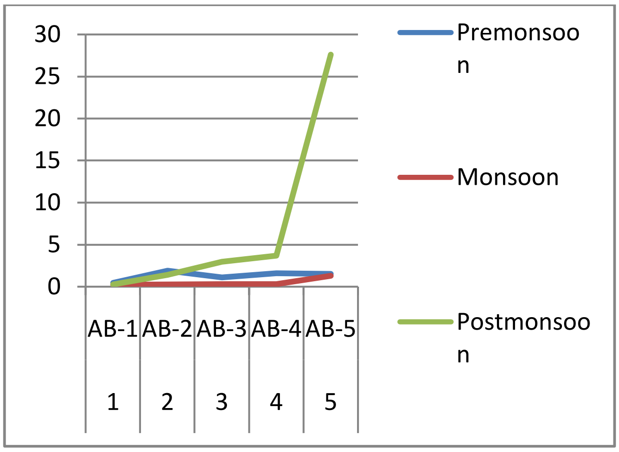
Parameters	I:S [2490-1974]	EPA[1987]	CPCB[2000]
pH	5.5-9.0	6.0-9.0	6.0-9.0
BOD	30	30	-
COD	250	250	-
Cu	3.0	3.0	3.0
Fe	3.0	3.0	3.0
Mn	2.0	2.0	-
Ni	3.0	3.0	3.0
Pb	0.1	0.1	0.1
Zn	5.0	5.0	5.0

Table 1: I:S, EPA and CPCB standards for discharge of industrial effluents in to inland surface waters

S.No.	Sites	Mar-Jun	Jul-Oct	Nov-Feb
1	AB-1	7.14	7.88	13.27
2	AB-2	7.76	7.74	4.16
3	AB-3	7.47	8.60	5.66
4	AB-4	7.03	8.63	5.09
5	AB-5	7.27	8.21	9.90

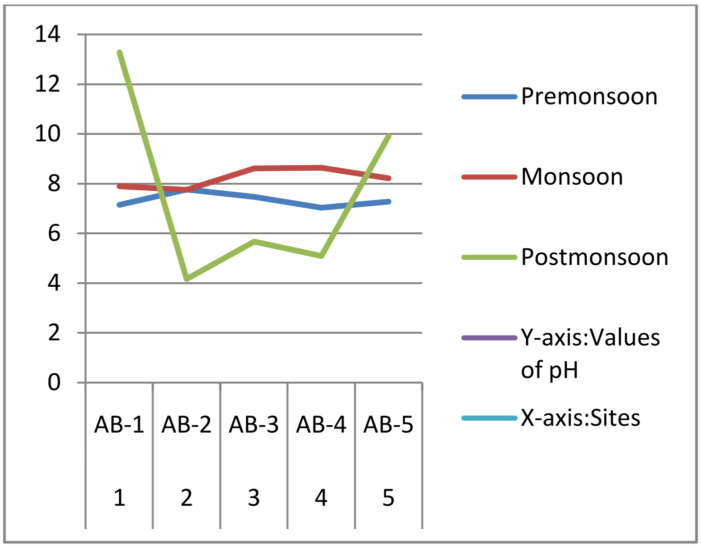
Table 2: Copper metal concentration in mg/l



Graph 2: Copper metal concentration during three seasons in all sites

S.No.	Sites	Mar-Jun	Jul-Oct	Nov-Feb
1	AB-1	7.14	7.88	13.27
2	AB-2	7.76	7.74	4.16
3	AB-3	7.47	8.60	5.66
4	AB-4	7.03	8.63	5.09
5	AB-5	7.27	8.21	9.90

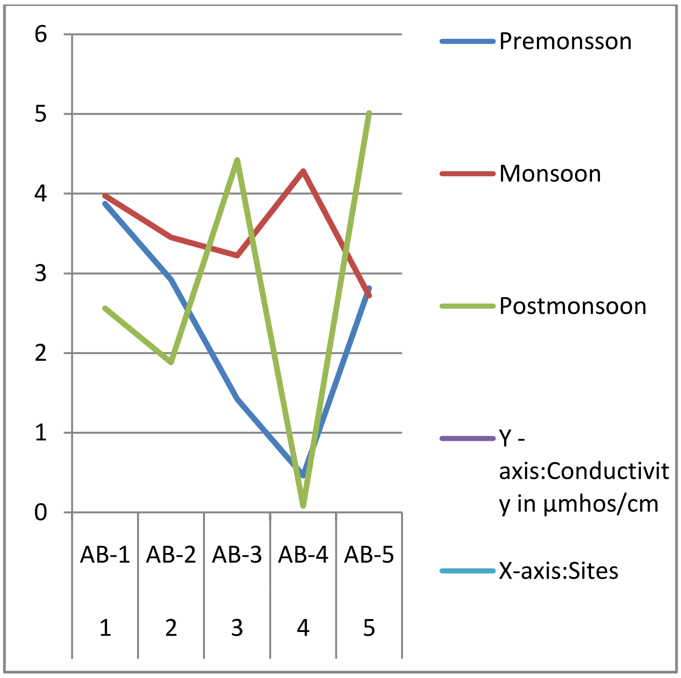
Table 3: pH during three seasons in all sites



Graph 3 : pH level during three seasons in all sites

S.No.	Sites	Mar-Jun	Jul-Oct	Nov-Feb
1	AB-1	3.87	3.97	2.56
2	AB-2	2.92	3.45	1.88
3	AB-3	1.42	3.22	4.42
4	AB-4	0.46	4.28	0.08
5	AB-5	2.81	2.72	5.01

Table 4: Conductivity in µmhos/cm

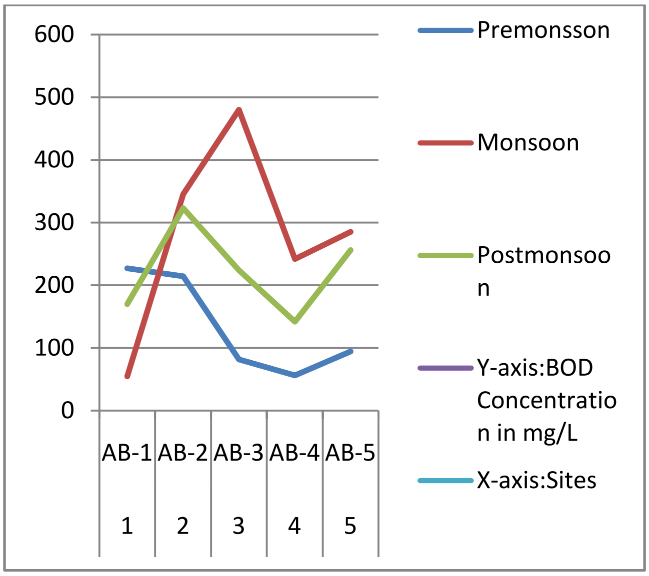


Graph 4 : Conductivity value during three seasons in all sites

International Journal of Scientific Engineering and Technology (ISSN : 2277-1581)
Volume No.3, Issue No.1 pp : 43-46 1 Jan 2014

S.No.	Sites	Mar-Jun	Jul-Oct	Nov-Feb
1	AB-1	227	54.85	170
2	AB-2	214	345.52	323
3	AB-3	81.6	480	224
4	AB-4	56.06	242	142
5	AB-5	94.5	285.14	256

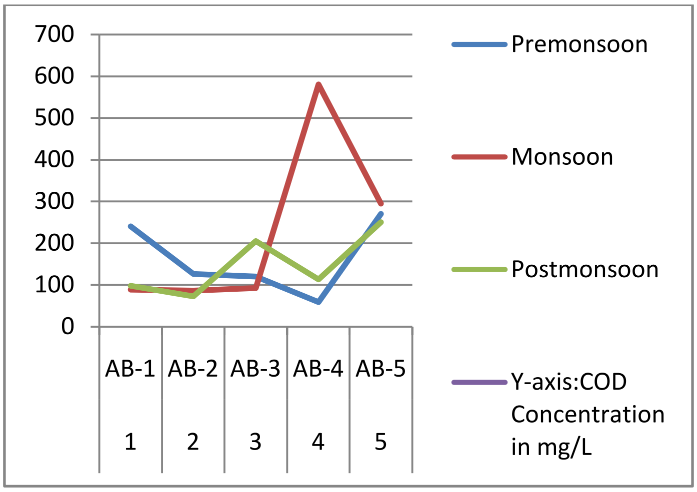
Table 5: Biological Oxygen Demand (BOD) in mg/l



Graph5: Biological Oxygen Demand concentration during three seasons in all sites

S.No.	Sites	Mar-Jun	Jul-Oct	Nov-Feb
1	AB-1	240	88	98
2	AB-2	126	86	72.62
3	AB-3	120	92	205
4	AB-4	58.45	580	112.82
5	AB-5	270	294	250

Table 6: Chemical Oxygen Demand (COD) in mg/l



Graph6: Chemical Oxygen Demand concentration during three seasons in all sites