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Removal of heavy metals from industrial effluents by water hyacinth (*Eichornia crassipes*)

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A study was carried out using water hyacinth as a pollution monitor for the simultaneous removal of heavy metals such as copper (Cu), cadmium (Cd), iron (Fe), zinc (Zn), lead (Pb), chromium (Cr) and aluminium (Al). Effluents were collected from eight industries including paint, textiles, aluminium, galvanizing and battery industries situated in Lagos State, Nigeria. After cultivation of the plant for seven days in a plastic bowl containing each effluent, while sampling was carried out from the bowl everyday, the collected samples were analyzed for Pb, Fe, Zn, Cr and Cu at wavelengths 248.3, 213.7, 357.9 and 324.9 nm respectively using atomic absorption spectrophotometry. Aluminium was determined using UV spectrophotometry and potassium was determined using a flame photometer. The results of the analysis indicated that the range of the heavy metal in the effluents before the cleaning process were Pb (0.1 to 4.4 ppm), Cr (0.39 to 0.5 ppm), Cu (0.08 to 1.65 ppm), Zn (0.7 to 8.7 ppm), Fe (1.2 to 7.5 ppm), Al (0.15 to 1.05 ppm) and Ni (0.6 to 49.2 ppm) while Cd was not detected in none of the effluents. The values were higher than the Federal Ministry of Environment and the World Health Organization effluent limitation guidelines recommended levels. The cleaning experiment showed that water hyacinth has the ability to clean-up the effluents of their heavy metals content by removing about 70 to 90% of their initial concentrations within four to six days of the experimental set-up.

Key words: Industrial effluents, heavy metals, water hyacinth, health impact, environmental pollution.

INTRODUCTION

Heavy metals are potentially toxic minor elements that may occur in low concentration or trace amounts in a given matrix. In the metallic state, they are relatively harmless but in vapor states, their fumes are toxic and so are their soluble compounds. Heavy metal pollution is a problem associated with the areas of intensive industrial activities (Kołodyńska, 2010) from where untreated effluents are introduced into the environment. The effluents usually contain toxic metals such as Cd, Hg, Ag, Pb, Sn and Cr, and others like Zn, Cu and Ni which are toxic at elevated concentrations (Sunda and Huntsman, 1998; Chojnacka et al., 2004). Some of these metals are found in effluents from hydrometallurgical, electroplating, tanning, artificial fertilizers and herbicides production as well as dyeing, textile, electrochemical, motor, energetic industries. The heavy metals can percolate into ground water and pose a significant threat to human health and ecological systems (Najafia et al., 2011). For example the tolerance limit for Hg(II) for discharge into land surface water is 10.0 µgL^{-1} and for drinking water is 1.0 µgL^{-1} (WHO, 1971). Concentrations above this level could lead to human health problems such as mammalian cancer and respiratory diseases. Also, chromium, commonly used in many industrial applications such as tanning processes, electroplating, pigmentation, wood presservation, or as catalyst for corrosion inhibition is a highly toxic metal and its release into the environment has become a serious health concern (Elangovan and Philip, 2009; Budavari, 1996). Chromium (VI) is more hazardous

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than chromium (III) due to its mutagenic and carcinogenic properties (EPA, 1980). Lead poisoning was associated with symptoms such as headache, irritability, abdominal pain and various symptoms related to the nervous system (Jarup, 2003), while cadmium, copper and zinc poisonings showed symptoms such as gastrointestinal disorders, diarrhea, stomatitis, tremor, ataxia, paralysis, vomiting, convulsion, depression and pneumonia (McCluggage, 1991).

Therefore the need for the removal or reduction of the levels of these toxic metals from industrial effluents before being discharged into the environment cannot be overemphasized. However, it suffices to mention that conventional methods for the removal of these heavy metal ions from effluents such as those based on ion exchange, precipitation, electrochemical treatment etc. are often faced with some drawback such as chemical derivatization, high cost of treatment, long reaction procedures which are time consuming, producing large quantities of chemical sludge and having poor specificity in the presence of other ions. Therefore, biological treatments have been identified in the recent time as an alternative technology because of their lower impact on the environment compared to chemical methods (Bulut and Tez, 2007; Jadhav et al., 2010; Gonc et al., 2009; Chatterjee et al., 2010; Wang and Chen, 2009; Maine et al., 2009).

Many researchers have reported the use of algae and bacteria species for concentrating metal species from dilute aqueous solutions and accumulating them within the structure of the microorganism (Wang and Chen, 2009; Maine et al., 2009; Mishra et al., 2009; Megateli et al., 2009; Rollemberg and Goncalves, 2000). These organisms can also remove heavy metal ions selectively (Megateli et al., 2009). Similarly, there are many reports on water hyacinth (*Eichhornia crassipes*) as highly effective biological plant in removing excess nutrients and heavy metals in fresh water body and metal solutions (Smolyakov, 2012; Mishra and Tripathi, 2009), waste water (Soltan and Rashed, 2003), polluted lake, river and water bodies (Chunkao et al., 2012; Tejeda et al., 2010). It has also been used as biosorbent for the removal of Cd(II), Pb(II) and Cu(II) ions from aqueous solution (Ibrahim et al., 2012; Zheng et al., 2009). The process of uptake of chemical species by water hyacinth may take place through the cell membrane via diffusion and osmosis. Uptake of metal ions from aqueous solution is by chelation of the metal ions with amino acid, carboxylic and hydroxyl groups (subunits) of macrocyclic molecules, such as ionophores present in the mitochondria of water hyacinth. This leads to the deprotonation reaction of water hyacinth during the process and consequently leading to decrease in pH of the growth media (Soltan and Rashed, 2003).

Lagos state is up till now regarded as the commercial capital of Nigeria where many manufacturing and industrial processes are taking place. This has led to the exodus of large number of people in and out of the country

to settle down or choose Lagos State as their second home. Consequently, a large amount of municipal and industrial wastes containing toxic metals are uncontrollably discharged into various environmental compartments. Such toxic metals can eventually percolate the ground water which, most times, serves as source of water for human consumption and can constitute health hazard.

This study was embarked upon to investigate the suitability of water hyacinth in checkmating the amount of heavy metals disposed to the environment through industrial effluents. If found suitable, water hyacinth, a biological organism, could reduce further pollution of the environment arising from using chemical techniques.

MATERIALS AND METHODS

Sample collection and preparation

Effluent samples were collected from eight different industries in Lagos, Nigeria in pretreated 25 L plastic bottles. Some of the effluents were collected directly from a waste tank in the factory while others were collected from a waste outlet that led directly outside from the production floor. The industries are: two aluminium industries, two paint industries, two textile industries and one battery and one galvanizing industry. The initial pH of the effluents was measured using JENWAY 3015 pH meter and recorded. Buffered solutions of pH 4.0 and 9.0 were used for pH meter's calibration.

One hundred completely uprooted water hyacinth (*Eichornia crassippes*) plants were collected from a lagoon under Mile-2 bye-pass bridge in Lagos. They were spread on tap water surface in three large bowls to which was added 20 g NPK (Nitrogen-Phosphorus-Potassium) fertilizer prior to commencement of the experimental set-up.

Reagents used and treatment of containers

Reagents used were of analytical grade (BDH chemicals) and include cadmium nitrate ($Cd(NO_3)_3.4H_2O$), aluminium nitrate ($Al(NO_3)_3).9H_2O$), aluminium metal, ammonium acetate, zinc sulphate ($ZnSO_4.7H_2O$), copper sulphate ($CuSO_4.5H_2O$), chromium chloride ($CrCl_3.6H_2O$), iron (III) nitrate ($Fe(NO_3)_3).9H_2O$), potassium chloride (KCl), sodium chloride (NaCl), lead acetate ($Pb(CH_3COO)_2.3H_2O$), gum arabic, p-nitrophenol and thioglycolic acid ($HSCH_2CO_2H$ or $C_2H_4O_2S$). Solutions were prepared using bi-distilled water. All glassware used were washed in detergent solution, rinsed several times with distilled water and then soaked for 48 h in 10% HNO_3, after which they were rinsed further with distilled water and dried overnight in an oven at a temperature of 120°C before used (Ogunfowokan and Fakanku, 1998). Two hundred of 120 mL plastic bottles needed for sampling from the industrial effluents were cleaned using (1:1) HCl-water solution, being then fully filled with the 1:1 HCl solution and left for 24 h, after which they were rinsed with distilled water and dried.

Experimental setup

Eight plastic bowls previously cleaned and dried using the acid treatment method described above, were each labeled A - H with each label corresponding to a particular industrial effluent. The bowls were rinsed with the effluents from each industry before the

Table 1. Working conditions of Buck scientific atomic absorption spectrophotometer for the analysis of heavy metals.

Metal	Wavelength (nm)	Slit width (nm)	Lamp current (mA)	Gain	Oxidant	Acetylene flow	Burner height	Detection limit (ppm)
Cd	228.8	3	2	7	Air	2.1	7	0.002
Cr	357.9	1	5	5	Air	4.7	5	0.002
Cu	324.7	2	4	5	Air	1.8	7	0.001
Zn	213.9	2	4	8	Air	13.5	7	0.006
Fe	248.3	1	8	8	Air	3.8	6	0.003
Pb	217.0	3	4	8	Air	2.4	6	0.004

Table 2. Initial concentrations (ppm) of the metals in the industrial effluents.

Industries	Cu	Cr	Cd	Pb	Fe	Zn	Al
Paint Industry-A	1.45	2.20	ND	ND	7.50	6.20	0.45
Paint Industry-B	1.10	2.30	ND	ND	5.40	2.50	0.45
Textile Industry-A	1.50	2.00	ND	1.00	4.55	5.30	0.55
Textile Industry-B	1.30	1.80	ND	1.40	4.10	5.40	0.45
Aluminium Industry-A	1.15	1.60	ND	0.60	5.20	2.80	1.05
Aluminium Industry-B	1.10	2.20	ND	0.80	4.80	2.50	1.05
Battery Industry	0.70	-	ND	4.40	4.00	6.10	0.83
Galvanizing Industry	1.65	3.90	ND	ND	5.00	8.70	0.83
FMEnv (1991)	<1.0	<1.0	<1.0	<1.0	20.0	<1.0	-
WHO (1984)	0.5	1.0	<1.0	1.0	15.0	1.0	-

ND: Not detected.

25 L content were finally turned into each bowl. Initial sampling was done by taking triplicate samples from each bowl using the 120 mL bottles. This initial sampling represents the initial concentrations of the heavy metals in each effluent before accumulation and monitoring using water hyacinth. To each of the bottles containing the effluents was added 5 mL of conc. HNO_3 to ensure that the metals do not adsorb onto the surface of the bottle but remain in solution. Five water hyacinth plants were placed in each bowl containing the effluent sample to start the accumulation and monitoring process. The sampling was done every 24 h for each setup representing a particular industrial effluent. The sampling process lasted seven days. Initial setup for the textile effluents indicated that the plant became yellow and withered after the third day due to the alkaline nature of the effluents (pH 9.3 and 12.6). Another set of experiment was setup for the textile industries after initially neutralizing the effluents by adding about 70 mL of conc. HNO_3 solution to bring the pH down to about 6.7.

Determination of heavy metal content

Each sample was wet digested with a 4:1 mixture of nitric acid and perchloric acid. The digested sample was evaporated to almost dryness and then made up to 100 mL with distilled water. 500 ppm standard solutions of the different metals were prepared from their respective salts. From each stock solution was prepared 1, 2, 3, 4 and 5 ppm of each metal for calibration study. Concentrations of the working ranges were obtained by diluting an appropriate volume of the stock solution (Bruce and Whiteshide, 1984). The concentration of the metals (Cd, Pb, Cr, Cu, Ni, Fe and Zn) was determined in an air-acetylene flame using atomic absorption spectrophotometer VGP Model 201 (AAS, Bulk Scientific East Norwalk, USA) available at the Centre for Energy Research and Development, Obafemi Awolowo University, Ile-Ife, Nigeria. The instrument working condition and parameters for the determinations are shown in Table 1. The equipment was previously standardized and corrected for background metal impurities using a blank determination. The samples were analyzed in triplicates (the relative standard deviation of the measurement was lower than 3%).

RESULTS AND DISCUSSION

Table 2 shows the initial concentration of the metals in the industrial effluents compared with Federal Ministry of Environment limitation regulations (FMEnv, 1991) and the World Health Organization maximum permissible limits in industrial effluents (WHO, 1984). Figures 1 to 8 presents the cleaning process as monitored by the plant (concentrations in mg/L). From Table 2, cadmium was not detected in any of the effluents, while the other metals occur at concentrations higher than the effluent limitation guidelines recommended by FMEnv. This implies that any unscrupulous and uncontrolled discharge of the effluents to the environment can impact significantly on the health of the inhabitants and the general biota considering the toxic nature of the metals.

Figures 1 and 2 present the metal pollution levels of the effluents from paint industries. Before the cleaning process, the metals were in the range: Cu (1.10 to 1.45 ppm), Cr (2.20 to 2.30 ppm), Fe (4.30 to 4.90 ppm),
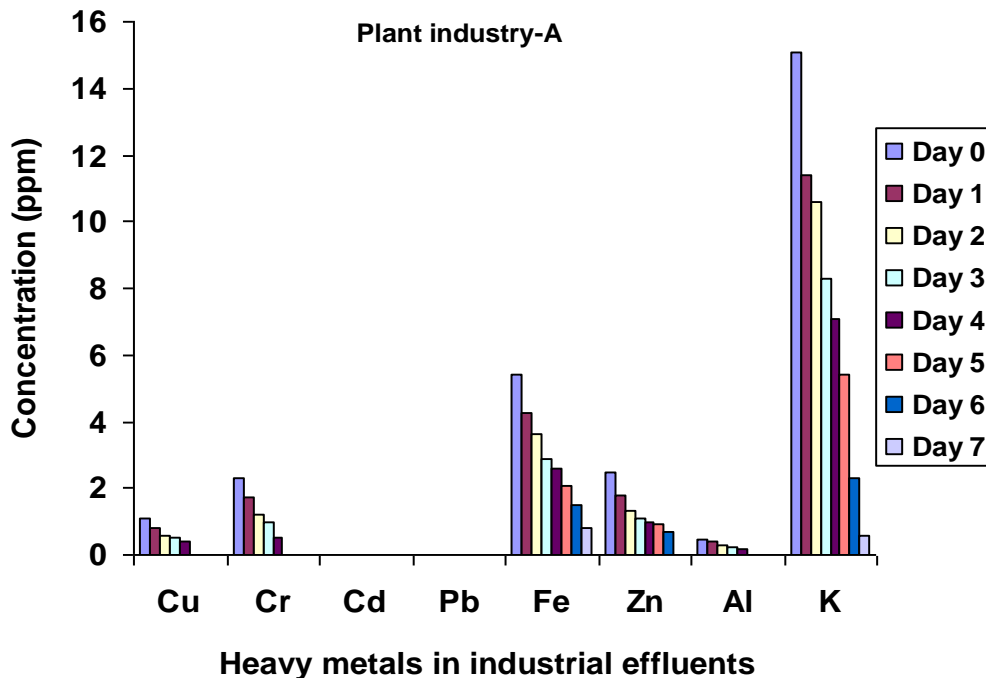
Figure 1. Paint industry-A (pH = 7.14): Mean concentration (ppm) of the heavy metals for the seven days cleaning process.
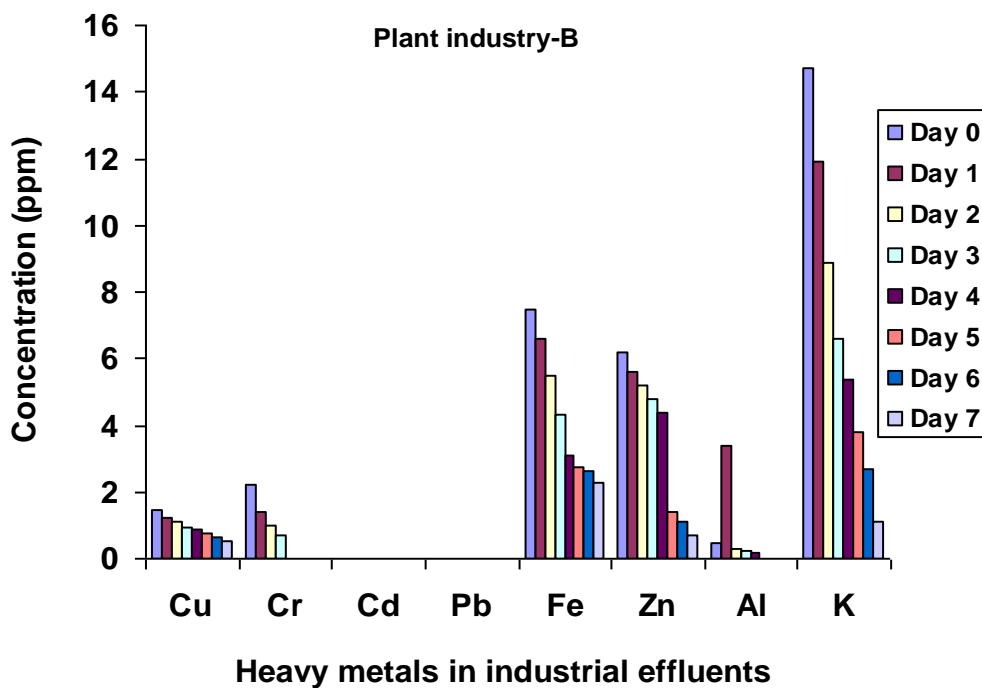

Figure 2. Paint industry-B (pH = 7.04): mean concentration (ppm) of the heavy metals for the seven days cleaning process.

Zn (2.50 to 6.20 ppm) while about the same value (0.45 ppm) was detected for Al in the effluents. Lead was not detected at all, while the prominence of the other metals could be attributed to the use of their oxides as pigments and binders in paint production (Budavari, 1996; Elangovan and Philip, 2009). Apart from the use of its
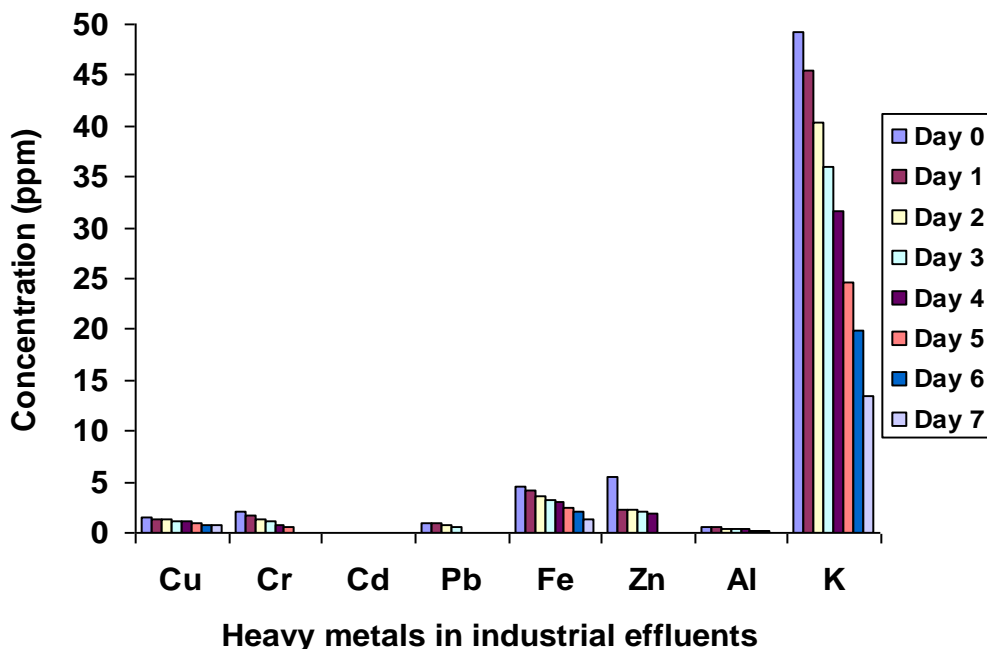
Figure 3. Textile industry-A (pH = 11.32 adjusted to 6.68): mean concentration (ppm) of the heavy metals for the seven days cleaning process.
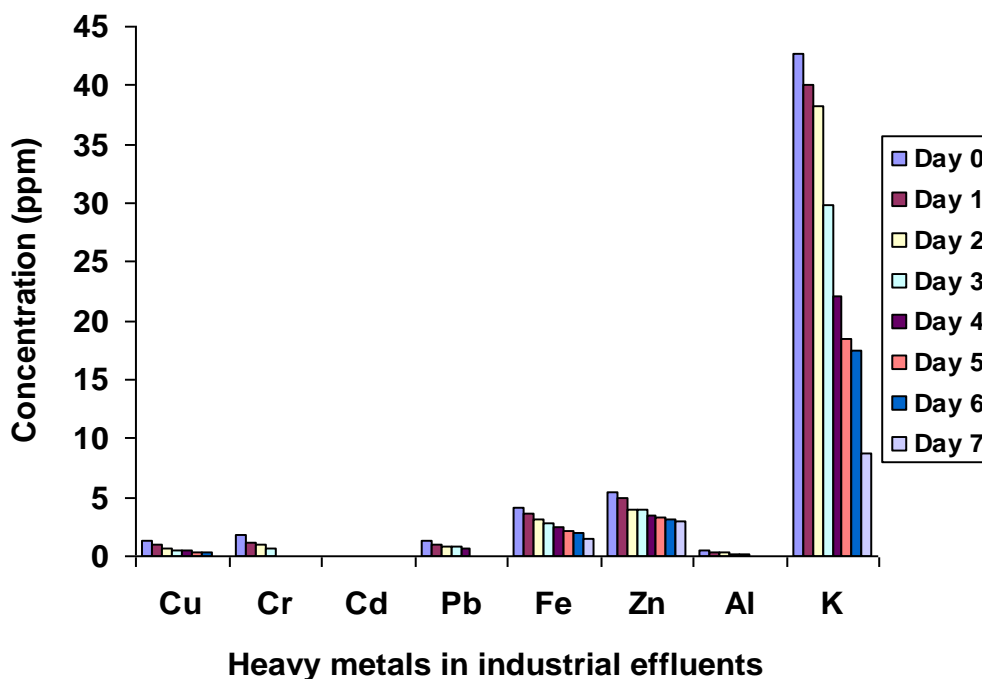
Figure 4. Textile industry-B (pH = 9.64, adjusted to 7.09): Mean concentration (ppm) of the heavy metals for the seven days cleaning process.

oxide as pigments, trace quantity of Al detected in these effluents, and the other effluents studied could be due to its use as pans, buckets and containers during industrial production processes. This is because of its light weight and therefore its substitution for iron made containers employed in the past. The ability of water hyacinth to clean up the heavy metals from the paint industries effluents was significant within the 7 days of the cleaning process. For example, from Figures 1 and 2, copper was reduced to zero in 5 days (paint industry A), chromium in
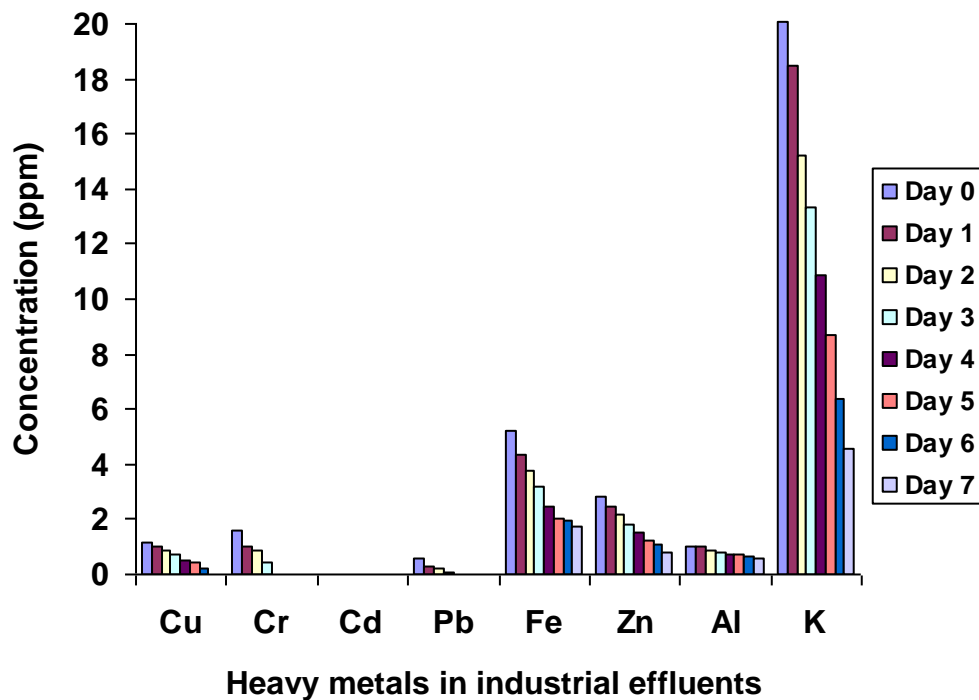
Figure 5. Aluminium industry-A (pH = 6.61): Mean concentration (ppm) of the heavy metals for the seven days cleaning process.
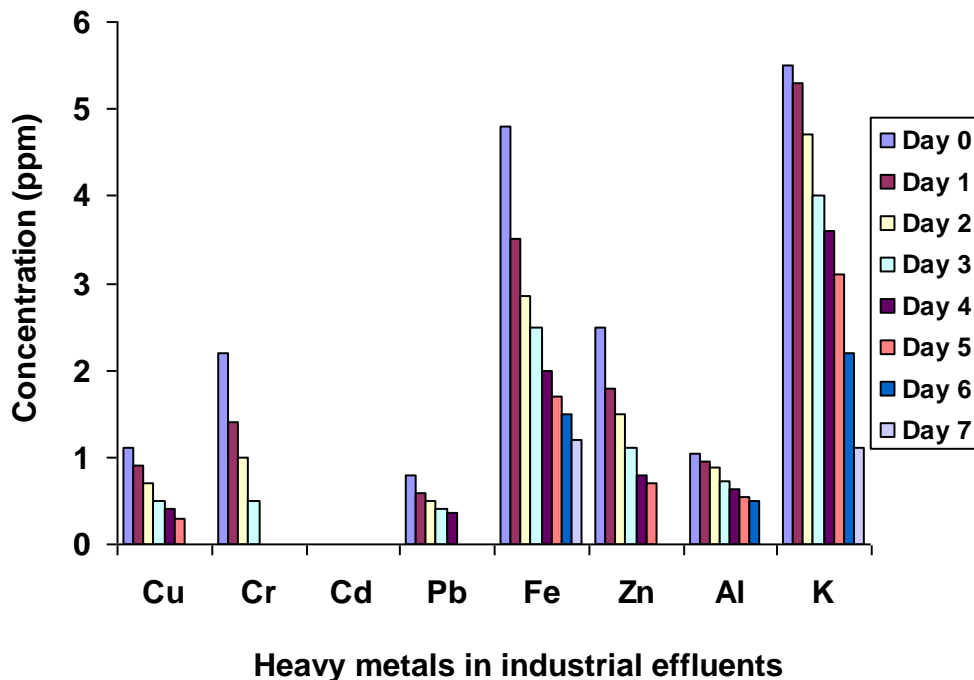

Figure 6. Aluminium industry-B (pH = 7.08): Mean concentration (ppm) of the heavy metals for the seven days cleaning process.

4 days (paint industry B), zinc in 7 days while iron was reduced by 70% of its initial concentration in 7 days.

Figures 3 and 4 present the levels of the heavy metals in the textile effluents. Zinc was found to be more
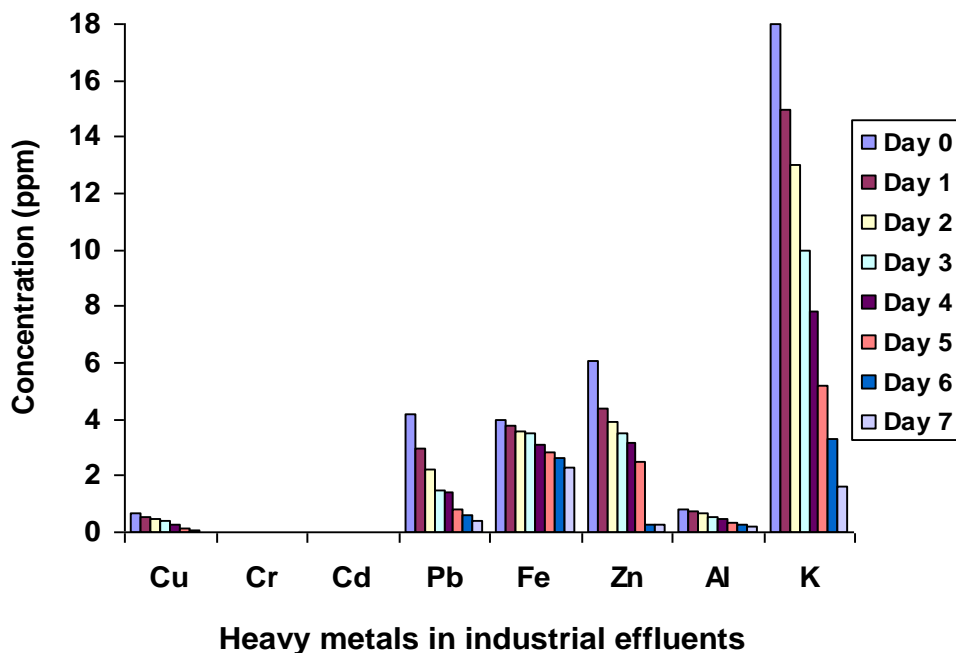
Figure 7. Battery industry (pH = 6.06): Mean concentration (ppm) of the heavy metals for the seven days cleaning process.
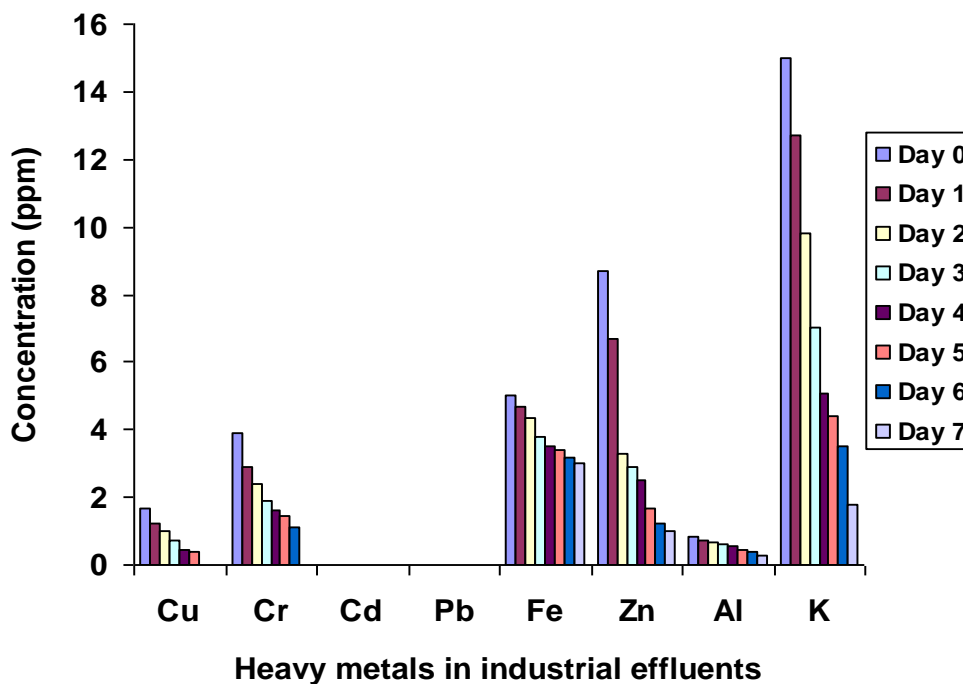

Figure 8. Galvanizing industry (pH = 7.14): mean concentration (ppm) of the heavy metals for the seven days cleaning process.

prominent (5.30 to 5.40 ppm) compared with the other metals. Concentrations of elements such as Cu (1.5 to 1.65 ppm), Cr (1.80 to 2.00 ppm), Pb (0.50 to 0.70 ppm), Fe (4.55 ppm) and Al (0.45 to 0.55 ppm) were particularly

worrisome especially that the effluents could be discharged without treatment to the environment. These values were higher than the effluent limitation guidelines recommended by both the Federal Ministry of Environment

(FMEnv, 1991), and the World Health Organization (WHO, 1971) maximum permissible limits in industrial effluents. Thus if left untreated, the heavy metals could pollute marine and other water bodies, percolate through the soil to the underground water, and finally endanger animal and human life. Therefore, making the environment heavy metals pollution free cannot be overemphasized. For example, Cr has been reported to cause mutagenic and carcinogenic effect (Jarup, 2003). Very high levels of zinc can damage the pancreas, disturb the protein metabolism and cause atherosclerosis (http://www.lenntech.com/periodic/elements/zn.htm#ixzz0 hgFRQvTx). Lead poisoning leads to headache, irritability, abdominal pain and various symptoms related to the nervous system (ATSDR, 2005). The involvement of these metals in textile production has been linked with the use of their oxides as mordant. However after the clean-up experiment (Figures 3 and 4), copper was reduced to about zero in 7 days, chromium was no longer detected within 4 - 6 days, zinc was cleaned-up of the effluents in 7 days while 31 % of iron remained in the effluents after the experiment.

In the aluminum industries effluents (Figures 5 and 6), the initial metal concentration before the clean up were: Cu (1.10 to 1.15 ppm), Cr (1.60 to 2.20 ppm), Pb (0.30 to 0.40 ppm), Fe (4.80 ppm), Zn (2.50 to 2.80 ppm) and Al (1.05 ppm). The significant amount of Al recorded compared with other effluents is not surprising as this was the major element used as raw material in the industry. On the other hand, the presence and the relatively low concentration of the other heavy metals in Al effluents compared with that recorded for paint and textile effluents can be attributed to the use of their oxides in low quantity especially to add colors and aesthetics to the different aluminum products. In these effluents, water hyacinth cleaned up Cu in 7 days, Cr in 4 days, Pb in 5 days, Zn in 6 days, while Fe was reduced by 75% in 7 days.

Battery industry effluent (Figure 7) contained 0.70 ppm Cu, 4.40 ppm Pb, 4.00 ppm Fe, 6.10 ppm Zn and 0.83 ppm Al. High concentration of lead (4.40 ppm) indicated clearly the use of lead cells in the industry. However, at the end of the experiment, Pb, Fe and Cu were cleaned up by 91% and Zn by 96%.

The results on galvanizing industry (Figure 8) revealed that the effluent contained 1.63 ppm Cu, 3.90 ppm Cr, 5.00 ppm Fe, 8.70 ppm Zn and 0.83 ppm Al. The high concentration of Zn (8.70 ppm) indicated the use of Zn as surface coating material in this industry. It was generally observed from all the results presented in Figures 8 that the ability of the plant to remove the metals within seven days depends on the initial concentration of the metals. However, metals with higher concentration after the seven days can still be further reduced to a tolerable level if the experiment was given more time. The general observations showed that at the end of the 7th day, about 70 to 90% of the metals have been successfully removed by the plant. The result is in agreement with Chigbo et al.

(1982) who had already established that water hyacinth can absorb high concentration of heavy metals over a relatively short period of time. The result agreed with the study conducted by Mishra and Tripathi (2009), where water hyacinth was used to remove 95% of zinc, and 84% of chromium from their solution during 11 days incubation period. In the same vein, study carried out by Smolyakov (2012) using water hyacinth revealed that after 8 days, the remaining amounts of metals relative to their initial concentrations for multi-metal pollution treatments were 8% (Cu), 11% (Pb), 24% (Cd), and 18% (Zn) at pH 8, which also compare favorably with the results obtained in our study. The results also agreed with other reports where water plants and other biological materials have demonstrated significant potential in removing heavy metals from industrial effluents (Mishra et al., 2009; Chojnacka et al., 2004; Jadhav et al., 2010).

Conclusion

The results obtained in this study proved that water hyacinth could satisfactory remove up to 70 to 90% of the heavy metal levels of an industrial effluent. Thus water hyacinth has effective and efficient cleaning properties and thus could be used to clean up industrial effluents in a pre-treatment tank before discharging into the city's water ways, streams, and rivers. Therefore the use of the plant can be an alternative and less expensive effluent treatment method that can be employed by many industries in a pre-treatment tank before final discharge of their effluents to the environment. Doing this will ensure a cleaner marine environment and avoid the problems of polluting edible marine creatures, especially.

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