Phytoremediation of Heavy Metals Concentration in Asa River using Water Hyacinth

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Abstract: *The level of heavy metals needs to be reduced to an incredibly low and acceptable level, the current research set out to investigate and quantify the amount of heavy metals being released into the Asa River in Ilorin as a result of nearby companies. Water hyacinth was used as a biosorbent to reduce the level of concentration of these heavy metals to a minimal level, and sections of the Asa River were studied to ascertain the results of effluent releases affecting water quality in terms of its physicochemical parameters and heavy metal concentration. Standard laboratory techniques were used to collect and analyze water samples from three distinct locations along the river's course for physicochemical and heavy metal components. Atomic Absorption Spectrophotometer (AAS) were used to determine the concentration of the metals, Fourtier-transform infrared analysis (FTIR), Scanning Electron Microscopy (SEM), and Energy dispersive X-ray (EDX) tests were also performed on the water hyacinth used as the heavy metal adsorbent. The findings demonstrated that the degree of pollution varied between sampling sites, that the water quality was tolerable at sampling site Upper stream (US) but became impaired in the Middle stream (MS) and relatively impaired in Lower stream (LS), indicating significant pollution from close-by industries, and that this pollution was reduced by using an aquatic plant (water hyacinth). Chromium metal ions in the Asa River were effectively removed by water hyacinth, particularly in MS and US and Cadmium in all the investigated sites. Depending on the contact time (24, 48, or 72 hours) at biosorbent dose (0.001g, 0.005g, 0.100g), The results thus revealed that the river's water may be adsorbed for use in agriculture and domestic use. Hence, it is recommended for industrial and domestic application.*

Keywords: Heavy Metals, Physico-chemical, FTIR, SEM and EDX, Adsorption Process, Water hyacinth, Asa River.

1. Introduction

Freshwater systems like rivers are essential to the continuation of life. They are valuable resources that are needed everywhere. The importance of these water networks to all living things cannot be overestimated due to their importance for human requirements, according to Roya Mousazadeh in 2013. One of the main rivers, the Asa, almost splits the city of Ilorin. Due to the indiscriminate discharge of untreated sewage, this river is extremely vulnerable to contamination. In addition to domestic waste and other activities that are conducted along it that cause pollution, it regularly gets waste from industries situated along its course. Even though the river is where industrial effluents are dumped, it still contains dangerous substances like oil, heavy metals, and other compounds that could harm the aquatic life that calls the water body home. Regarding this, aquatic plants and animals are also affected because pollution primarily disrupts and interferes with their regular population dynamics and functioning. Given how dependent man is on fresh water resources for survival, all these effects will eventually be felt by man. Man is therefore vulnerable to the issues presented by threats. Even with the government's increased efforts to raise public awareness, water pollution still has a negative impact on community development and health, and it must be kept to a minimum so that, after treatment, the water can be used effectively for drinking and domestic purposes and to lessen the effort required to provide water for community development.

Therefore, this study seeks to investigate the water quality at three separate sample locations along the Asa River's course as well as the application of phytoremediation techniques for reduction or total elimination of identified heavy metals.

2. Materials and Methods

Description of the Study Area
Three points, upper stream, middle stream, and lower stream, are used in this study. The area's general population gets their water primarily from these water sources. The three sampling locations chosen for this study, as shown in Figure 1, were broadly the same as those reported by Olayemi *et al.*, 2003 and Ogundiran and Fawole in 2014 regarding the potential for heavy metal contamination. Ilorin's socioeconomic development benefits from and depends on the river. Along its bank and its tributaries, the town's major industry is located.

Three sampling sites (US, MS and LS) were chosen for this investigation based on the different industrial effluents being discharged into the river, Lower stream point (US) has relatively low level of human activities and was taken as control, middle stream point (MS) has the effluent discharged from a pharmaceutical industry flowing directly to the river and lower stream point (LS) has a very busy highway runoff water and a flow of effluent discharged from metal fabrication industry. Subsequently, the aforementioned sampling points were chosen based on

Plate 1: The plate showing Water at LS, MS and US

The proximity to nearby companies, how swiftly they receive their effluents, how much pollution they produce, and how far they are from the industrial sites.

Sample Collection and Analyses
Three sampling stations at varied distances from the source of the effluent flow were used to collect water samples and it is done in triplicate. The polyethylene bottles that were used to collect the samples were cleaned, rinsed with a weak solution of nitric acid, then rinsed two or three more times with some of the water that had been sampled and later analysed for physicochemical and Heavy metal concentration using Atomic Absorptive Spectrophotometer (AAS)

Water hyacinth (*Eichorniacrassipes)* was obtained from Ogudu lagoon in Lagos State as shown in plate 2a. The plant was transported into the laboratory in a sterile polythene bag containing water obtained from the collection site. The plants was washed severally with distilled water to

Plate 2 (a): The plate showing water hyacinth b: the adsorption process.

get rid of impurities and other epiphytes, sundried for 168 hours (7 days) and by using a blender to crush into powder, and then sieving with a fine mesh siever, (laboratory test sieve of 100mm pore size) according to Adewoye *et al*., 2021. The test solutions were produced by diluting a stock solution with a 1000 mg/l concentration of Cu, Cd, Pb, Zn and Fe to the required concentrations. Each test solution's pH was brought to the desired level (pH of 7) by being diluted with Hcl and concentrated with NaOH solution prior to adding the adsorbent. Experiment was carried out according to Adewoye *et al.,* 2021 for each stock solution, 40 ml of each of the stock solutions were weighed in the plastic bottles with different concentrations of the absorbent, the absorbent was allowed to interact with the metals in different time intervals of 24, 48 and 72 hours

Adsorption experiment was carried out according to Adewoye *et al.,* 2021. Different concentration of each substrates (0.001g, 0.005g and 0.010g) was weighed in 40 ml of the water samples. Each absorbent was allowed to interact with the metals in the water samples for different time intervals of 24, 48 and 72 hours as shown in plate 2b

Scanning electron microscopy (SEM) analysis was carried out on the water hyacinth samples, to assess its morphology

on the surface and elemental composition of initial materials using JEOL JSM-6390model scanning electron microscope coupled with energy dispersive X-ray (EDX) analyzer. Although SEM has a high resolution, it is feasible to magnify materials that are close together. According to Mohamed and Amaal, 2017, Olakunle *et al*., 2017, and Bello *et al*., 2017, diffuse Fourier-transform infrared analysis (FTIR) was used to characterize carbonaceous materials of the adsorbates in order to qualitatively determine the functional groups in frequency ranged between 4000 and 400 cm-1 at room temperature.

A mercury-filled thermometer was used to measure the temperatures. The thermometer was lowered vertically into the samples, after the mercury indicator had been steadily stable and readings recorded (APHA, 1998, Taylor, 2000, Kesalkar, *et al*., 2012).

Prior to conducting the test, with the aid of the recommended buffer solutions, the pH meter was calibrated. After dipping the pH probe into the samples' water until an accurate reading was made, the pH of each sample was measured. The probe was washed with de-ionized water after each measurement to prevent contamination of additional samples while determining the pH of those samples (APHA, 1998, Ademoroti, 2001: Dalal *et al*., 2013, Alexander Decker, 2013).

Total Dissolved Solids
It was calculated using the gravimetric method by drying a known volume (50 ml) of water in a crucible that had already been weighed on a steam bath. The difference between the crucible's pre-weighed weight and the beaker's weight after drying will be recorded as (W_2g-W_1g) (APHA, 1998, Medudhula *et al*., 2012, Alexander Decker, 2013, Ahaneku and Animasahun, 2013, Ogundiran and Fawole, 2014).

Then Total Dissolved Solids was calculated as

$$\frac{W_{2g} - W_{1g} \; 1000 \; X \; 1000}{Vol \; .of \; Sample}$$

Conductivity
Using a conductivity meter (model HI 98130 HANNA), this was determined. The sample's conductivity was assessed together with the calibration of the probe. After allowing the readings to stabilize, the probe was lowered into the samples, and the results were then recorded. After measuring each sample, the probe was rinsed with de-ionized water to prevent contaminations (APHA, 1998, Ademoroti, 2001, Medudhula *et al*., 2012, Dalal *et al*., 2013, Ahaneku and Animasahun, 2013, Ogundiran and Fawole, 2014).).

Dissolved Oxygen
The water of 2ml each was placed in bottles, 2ml of $MnSO_4$ solution and 2ml of alkali-iodide-azide reagent been added to the samples, air bubbles was excluded with care before thorough mixing of the reactants by severally inverting the bottles until clear supernatant water was obtained. It was then given two minutes to settle. Following the addition of 2 ml of concentrated H2SO4, the reaction was allowed to foam before being gently stirred by inversion until dissolution was complete. Iodine of 5ml was added

uniformly. The solution was decanted and later titrated with 0.0125M $Na_2S_2O_3._5H_2O$ (APHA, 1998, Medudhula *et al*., 2012, Ahaneku and Animasahun, 2013, Ogundiran and Fawole, 2014).

Biochemical Oxygen Demand
Biochemical Oxygen Demand was estimated using the dilution method. The samples' dissolved oxygen content was assessed both before and after five days at 200C of incubation. After dilution was taken into account, the difference provides the BOD of the samples (APHA, 1998, Kesalkar, *et al*., 2012, Alexander Decker, 2013).

Total Hardness
Twenty five mililitres of sample was diluted to 50ml with distilled water in a conical flask, 1ml of buffer solution was added and it will be titrated, slowly with continuous shaking until reddish colouration disappears after which few drops of Ethyl diamine tetra acetic acid (EDTA) was added at 3-5 seconds intervals and the result was recorded (APHA, 1998, Medudhula *et al*., 2012, Alexander Decker, 2013, Ahaneku and Animasahun, 2013, Ogundiran and Fawole, 2014).).

Total Alkalinity
Fifty mililitres of sample was placed into a clean conical flask and a drop of 0.05M sodium thiosulphate solution was added in order to remove free chlorine residue that may be present in the samples. Two drops of phenolphthalein indicator was added to samples and later titrated the solution with 0.02M standard of HCl until the colour disappeared (APHA, 1998, Ademoroti, 2001, Dalal *et al*., 2013, Alexander Decker, 2013)

Turbidity
A turbidity meter was used to measure the samples' turbidity (model 2100P Turbidimeter HACH). After each sample had been stabilized for 5 minutes in the sample container, the reading was taken and recorded (APHA, 1998, Taylor, 2000, Medudhula *et al*., 2012,).

Metals evaluation in water
Fifty millitres of each of samples was taken, filtered through Whatman filter paper, acidified with concentrated HNO_3 in order to reduce the pH, thereafter 40 ml of sample was taken and 5 ml concentrated HNO_3 was added, digested in a closed chamber for 30 minutes. It was then be made to 100 ml with distilled water. The digested samples were analyzed for metal concentrations by Atomic Absorption Spectrophotometer (Perkin Elmer 3110) (Morris, 2005, Dagne, 2020, Juan and Lilian, 2012, Ahaneku and Animasahun, 2013, Ogundiran and Fawole, 2014).

3. Results and Discussion

Water Analyses
Analysis and statistical comparisons of water samples from the US, MS, and LS were done, as well as comparisons with the World Health Organization (WHO), the National Environmental Standards and Regulations Enforcement Agency (NESREA), and the National Industrial Standards (NIS). To assess the degree of pollution in those areas, water samples were taken in triplicate and tested for a variety of physicochemical and heavy metal parameters. The studied

physicochemical parameters analyzed include pH, water temperature, dissolved oxygen (DO), turbidity, electrical conductivity (EC), total hardness and Alkalinity. Among heavy metals analyzed are Chromium (Cr^{3+}), Nickel (Ni^{2+}), Zinc (Zn^{2+}), Lead (Pb^{2+}), Copper (Cu^{2+}), Iron (Fe) and Cadmium (Cd). The findings of the analysis of water samples from the three sampling sites and the mean values of each parameter are shown in Table 1 for physicochemical and heavy metals: Mean values of datas were presented as average value of three triplicates (Mean +SEM). Mean value with the same alphabet are not significantly different from each other, values with different alphabet or superscript are significantly different. The samples observed at the locations and were recorded with higher temperatures of 26.00+0.58a at the upper stream, 26.67+0.33a at the lower stream and minimum value of 25.67+ 0.33a at the middle stream when compared with the standard of WHO 2011.

Hydrogen ion concentration of the water samples from the located sites had significant difference the samples were also observed and recorded at the collection site with high acidic value of 3.20+0.23a for the lower streams and 6.10 + 0.58b and 6.57 + 0.18b for middle and upper streams respectively. The EC values obtained in the upper, middle and lower streams were 1.43+ 3.25a, 2.07+ 3.60a and 2.19+ 4.24a respectively with higher values compared with the standard limit of USEPA of 0.05 Scm-1. The DO observed in all the located sites were higher than the standard limit of USEPA with the highest value of 39.17+ 3.51b at the middle streams and 36.27+ 0.73b at the lower streams with the minimum value of 6.70 + 1.56a at the upper streams. The variation of the values obtained in the hardness of the located sites were with higher values of 191.00+4.53a, 236.33+21.85a and 795.67+182.30b of upper, middle and lower streams respectively when compared with the standard limit of USEPA of 100 mg/l. The variation of the values obtained in the alkalinity of the located sites were with lower values of 306.00+23.02a, 410.67+13.53b of upper, middle and higher value of 649.33+33.50cof lower streams respectively when compared with the standard limit of USEPA of 500 mg/l. The turbidity values observed in the located sites were visibly turbid as it ranges from 14.05 to 19.59

The mean variation observed for Fe in the upper stream has the lowest concentration of 2.001+0.51a with mean value of highest concentration in lower stream of 35.660+13.93b and middle stream of 10.764+3.30a with significant difference in all the located sites when compared with WHO 2011. The variation observed in upper stream of 0.051+0.86a has the highest value with no significant difference when compared with the standard of WHO 2011, middle stream of 0.062+0.053a and lower stream of 0.04+0.10a. The mean variation observed for Zn in the middle stream has the lowest concentration of 1.172+0.32a with mean value of highest concentration in upper stream of 2.123+1.62a and lower stream of 0.015+0.64a with significant difference in the lower stream and no significant difference in the upper and middle stream when compared with WHO 2011. The mean variation observed for cd in the middle stream has the lowest concentration of 0.020+0.08a with mean value of highest concentration in middle stream of 0.022+0.01a and upper stream of 0.021+0.06a with significant difference in all the located sites when compared with WHO 2011. The mean variation observed for Cr in all the located sites were with no significant difference of 0.240+0.01a, 0.278± 0.01a and to 0.084±0.01a for US, MS and LS respectively when compared with WHO 2011. The mean variation observed for Pb in all the located sites were with no significant difference of 0.00+0.00a when compared with WHO 2011. The mean variation observed for Ni in the uppert stream has the highest concentration of 0.87+0.44a with mean value of lowest concentration in middle stream of 0.10+0.06a and lower stream of 0.11+0.06a

The functional groups present on water hyacinth was also determined using FT-IR spectrophotometer and five distinct strong peaks were observed on the spectra at 2356.62, 1714.19, 1626.00, 1447.59, and 1034.00 as shown in figure 1.

The scanning electron microscopy carried out on Water hyacinth revealed a surface coated with lignin structure as shown in plate 3a. The energy dispersive X-ray revealed the elemental composition, showing the presence of nine elements (O, C, Ca, Fe, K, Ag, Al, Si, Mn) with silicon having the highest weight of 72.45%, followed by silver (Ag) 9.55% and Potassium having the lowest weight of 1.24% in plate 3b
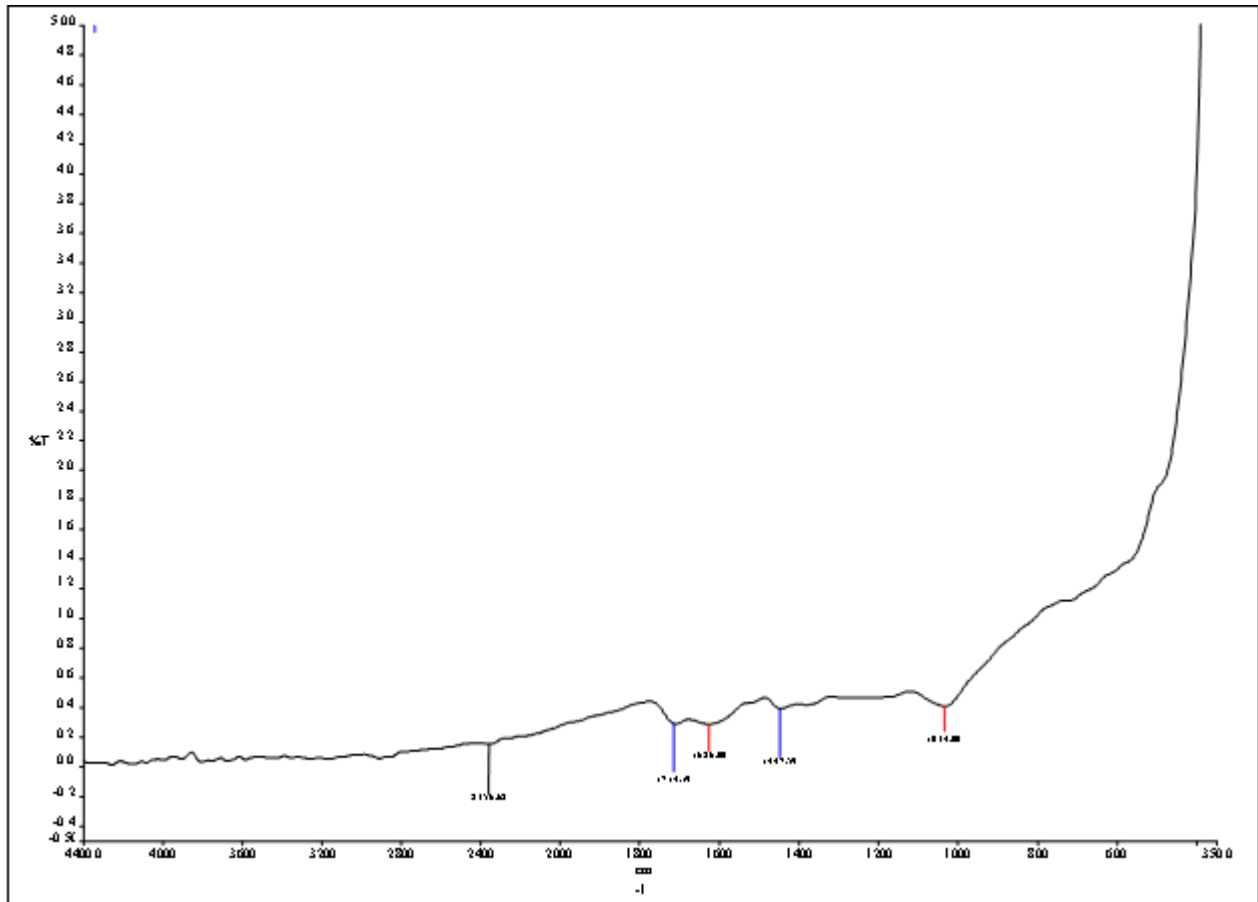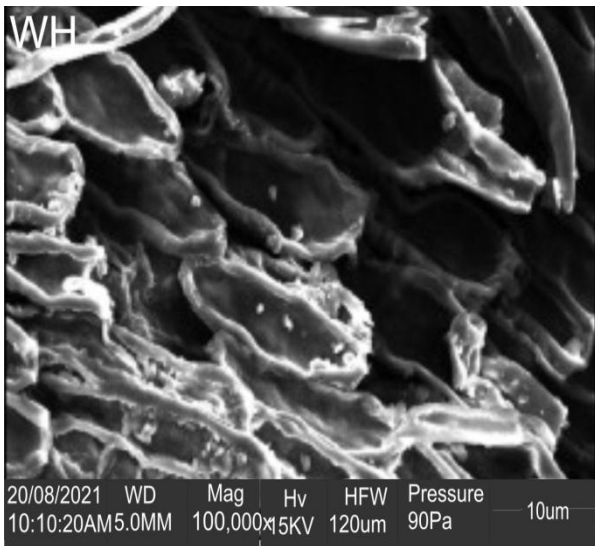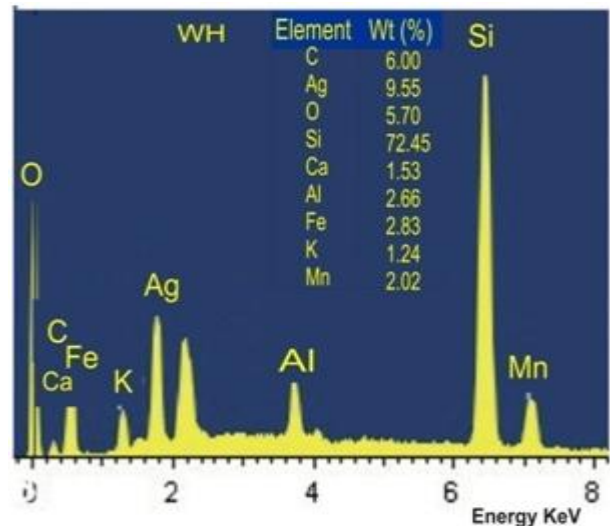
Figure 1: FT-IR result of Water Hyacinth

Plan 3 (a): SEM of Water Hyacinth.

Plan 3 (b): EDX of Water Hyacinth

Using water hyacinth as a bio-sorbent in the removal of heavy metals from Asa, river at varying concentration (0.001g, 0.005g and 0.010g) and contact time (24hrs, 48hrs, and 72hrs), there was a reduction in the concentration of the heavy metals. The maximum reduction of Fe in LS, at 24hrs, the concentration of Iron reduced from 35.660mg/l to 4.356mg/l, 3.452mg/l and 3.904mg/l at 0.001g, 0.005g and 0.010g of the bio-sorbent respectively (Table 1). Water hyacinth was efficient as a bio-sorbent in the removal of copper at varying concentration (0.001g, 0.005g and 0.010g) and contact time (24hrs, 48hrs, and 72hrs) in US and varying

concentration of 0.001g and 0.005g of 24hrs and 48hrs in MS with an exception in LS, where there was an increase in the concentration of the metal after the addition of the bio-sorbent.

Table 1: Concentration of Iron present in the water samples treated with water hyacinth

Iron (Fe)	WH			STD
	LS	MS US	WHO	
Initial conc. (mg/l)	35.660	10.764	2.001	0.300
0.001g (24hrs)	4.356	7.251	0.468	
0.005g (24hrs)	3.452	7.604	0.502	
0.010g (24hrs)	3.904	7.134	0.992	
0.001g (48hrs)	9.102	4.978	0.503	
0.005g (48hrs)	3.457	7.278	0.511	
0.010g (48hrs)	8.123	8.426	0.582	
0.001g (72hrs)	4.917	3.006	0.798	
0.005g (72hrs)	3.856	7.546	0.632	
0.010g (72hrs)	6.423	8.364	0.867	

Table 2: Concentration of Copper present in the water samples treated with water hyacinth

Copper (Cu)	WH			STD
	LS	MS	US	WHO
Initial conc. (mg/l)	0.015	0.062	0.057	0.01
0.001g (24hrs)	0.053	0.052	0.031	
0.005g (24hrs)	0.039	0.057	0.024	
0.010g (24hrs)	0.067	0.037	0.035	
0.001g (48hrs)	0.049	0.056	0.027	
0.005g (48hrs)	0.051	0.070	0.022	
0.010g (48hrs)	0.050	0.068	0.017	
0.001g (72hrs)	0.049	0.054	0.030	
0.005g (72hrs)	0.036	0.073	0.025	
0.010g (72hrs)	0.068	0.069	0.029	

Table 3: Concentration of Zinc present in the water samples treated with water hyacinth

Zinc (Zn)	WH			STD
	LS	MS	US	
Initial conc. (mg/l)	2.852	1.172	2.123	0.003
0.001g (24hrs)	0.376	0.570	0.085	
0.005g (24hrs)	0.390	0.581	0.091	
0.010g (24hrs)	0.572	0.620	0.213	
0.001g (48hrs)	0.334	0.527	0.085	
0.005g (48hrs)	0.379	0.557	0.063	
0.010g (48hrs)	0.374	0.635	0.115	
0.001g (72hrs)	0.395	0.663	0.180	
0.005g (72hrs)	0.373	0.528	0.090	
0.010g (72hrs)	0.440	0.625	0.243	

Table 4: Concentration of Chromium present in the water samples treated with water hyacinth

CHROMIUM (Cr)	WH			STD
	LS	MS	US	
Initial conc. (mg/l)	0.084	0.278	0.240	0.10
0.001g (24hrs)	0.000	0.000	0.000	
0.005g (24hrs)	0.000	0.000	0.000	
0.010g (24hrs)	0.000	0.000	0.084	
0.001g (48hrs)	0.000	0.000	0.000	
0.005g (48hrs)	0.000	0.000	0.000	
0.010g (48hrs)	0.000	0.000	0.000	
0.001g (72hrs)	0.000	0.000	0.000	
0.005g (72hrs)	0.000	0.000	0.000	
0.010g (72hrs)	0.000	0.000	0.000	

Table 5: Concentration of Cadmium present in the water samples treated with water hyacinth

CADMIUM (Cd)	WH			STD
	LS	MS	US	
Initial conc. (mg/l)	0.020	0.022	0.021	0.003
0.001g (24hrs)	0.000	0.000	0.000	
0.005g (24hrs)	0.000	0.000	0.000	
0.010g (24hrs)	0.000	0.000	0.000	
0.001g (48hrs)	0.000	0.000	0.000	
0.005g (48hrs)	0.000	0.000	0.000	
0.010g (48hrs)	0.000	0.000	0.000	
0.001g (72hrs)	0.000	0.000	0.000	
0.005g (72hrs)	0.000	0.000	0.000	
0.010g (72hrs)	0.000	0.000	0.000	

4. Discussion

Physicochemical Parameter in Water

Water is an important resource because of its availability, quantity, and quality in supporting both aquatic life and people (Fawole *et al*., 2008). According to Venkatesharaju *et al*., 2010, the physicochemical and natural qualities of water help to clarify its characteristics. Any environment's water quality can provide exact information on the sources needed to sustain and provide for ecosystem life. The results of this investigation showed that physicochemical variables of US like temperature, electrical conductivity, pH, dissolved oxygen, turbidity, hardness and alkalinity concentrations for the located sites samples were conformed with the standard of WHO 2011 and also supported by Ashok *etal*., 2006. The temperature values obtained were within the permissible limit within the range of 20-32°c recommended by Federal Environmental Protection Agency (FEPA), 1991 and range of $< 40^o$c recommended by World Health Organization (WHO), 2011, with maximum permissible limit. Ashok *et al*., 2006, Olorunfemi and Gabriel, 2018, Ahaneku and Animasahun, 2013 and Ogundiran and Fawole, 2014 also reported that the same range of temperature was observed in the Asa, river. The mean temperature in lower stream (LS) may be because of the effluent being produced and discharged from a steel production company that was very close to the located site around the vicinity, observation similar to this was also observed by Shankhadarwar, 2015. Because it affects the aquatic life forms that make up the ecosystem, a water body's pH is extremely important (Tepe and Boyd, 2002), it also controls the most important metabolic processes like respiration, in which living organisms produces energy useful for their day to day activities. pH values recorded for upper Stream (US) and Middle Stream (MS) were within the permissible limit of 6.0-9.0 except the LS of mean value of 3.20$\pm$ 0.23 as recommended by FEPA (1991) and WHO (2011) standard for river waters, also Ndimele and Kumolu-Johnson, 2012 reported low value compared with the standard. The adverse effect of pH results in LS substantiates with the study completed by Sharma *et al*., 2004 and Ogunwemimo and Osuala, (2004) in an estuarine rivers and an artificial lake in lagos and Ogidiaka *et al*., 2012 in Ogunpa river at Bodija, Ibadan. pH changes has significant effect of biochemical and chemical responses as reported by Simpi *et al*., 2011. The decrease in value of pH in LS may be due to increase in photosynthetic activities which increases the assimilation of carbondioxide and bicarbonate which were consequently responsible for its

decrease value as observed in LS and this suggests that carbodioxide, carbonate-bicarbonate is being affected lesser due to some particles from the steel production company. Azrima *et al*., 2011 state that the vast variations in the electrical conductivity of water's values are not typically known. Scatena, 2000 clarified the distinctions in relation to different components and usage of water. For instance, farming which brought out the mineral substances and in this manner the electric conductivity of the water was achieved. Conductivity does not have cordinate adverse effect on human wellbeing. It is then concluded for a few reasons as Kavcar *et al*., 2009 and Khan *et al*., 2013 concluded that assurance of mineralization rate in calcium and sodium was gotten by the conductivity of the water. If water with high conductivity is used for drinking, it may quickly lose its aesthetic appeal by tasting mineralized. Water with high conductivity may bring depreciation of metal surfaces of hardware for instance, an evaporator. It is additionally suitable to home appliances for example, water radiator framework and fixtures. Nourishment plant and environment framing plant species are additionally dispensed with the top conductivity (Katsoyiannis and Zouboulis 2013; Heydari and Bidgoli, 2012) and these generally serve as sustenance for aquatic life forms. Furthermore, the effect of high electrical conductivity may incorporate unsettling influences of salt and water adjust and large amounts of salt more often prompts increment in saltiness of water bodies which may resulted in antagonizing the natural consequences for aquatic biota. According to FEPA, the maximum permissible level of conductivity is 10, 000μS/cm while for WHO 2006, Standard, the maximum permissible limit is 25μS/cm. The mean value for electrical conductivity of the located sites were within the permissible limits range when compared with the standard of FEPA and WHO. Dissolved Oxygen is one of the most essential factors to be recone with in river and streams health as reported by Vankatesharaju *et al*., 2010. It is mostly relies on natural and wastewater of physical, chemical, biological exercises in the water bodies. Dissolved oxygen content assumes an important part in supporting aquatic life and is defenseless to slight environment changes. DO is additionally an imperative immunological parameter demonstrating the level of water quality and natural contamination in water bodies (Wetzel and Likens, 2006). The inadequancy of DO directly changes the biological community of a waterway because of bioaccumulation and biomagnification (Vankatesharaju *et al*., 2010). The mean value of DO in MS and LS jeered up from the standard of FEPA of 10 mg/l, the high value obtained was because of the result of the rate of photosynthesis by some plants in the water and this was also reported by Arimoro *et al*., 2008 in River Warri, Delta state. Total hardness is a parameter of water quality used to determine the effect of dissolved minerals deciding appropriates of water for domestical and drinking purposes and also indicate or affect the health of aquatic organisms because it controls the osmoregulation of the organisms. Hardness is the combination of the grouping of divalent metal particles for example calcium, magnesium, iron and Zinc, majorly obtained as water passes through the rock. In most water, it contains the most part of calcium and magnesium salts with trace element of different metals. The mean values of hardness obtained were greater than the permissible limit of FEPA. High alkalinity is a measure of water strength, it shows the capacity of wastewaters to neutralize acids, and is undesirable. The alkalinity of water may be caused due to OH^-, CO_3^{2-} and HCO_3^- ions. Alkalinity is the estimate of ability of water to resist change in pH upon addition of acid. Phenolphthalein and total alkalinity as $CaCO_3$ were found to be 306.00 ± 23.02 mg/lit in US, 410.67 ± 13.53 mg/lit in MS and 649.33 ± 33.50 mg/lit in LS respectively as also reported by Tekade *et al*., 2011. The turbidity is a characteristic of water that does not stable with the joined impact of shading and transparency. It measures the depth to which light enters in the water body. Turbidity likewise penetrates with the entrance of light and this reduces photosynthesis and subsequently reduces the essential profitability of a water body. Turbidity is the cloudness of water formed by an assortment of particles and is another important parameter in investigating water, such particles incorporates soil particles like earth and sand. algae, microorganisms and different substances. It is additionally known with the substance of infections creating life forms in water which may originate from soil overflow or runoff (Rahmanian, 2015). Higher mean values of turbidity expand water temperatures on ground because suspended particles retain more warmth which in turn reduces the concentration of dissolved oxygen because warm water holds less DO than cold water. In this present study, the mean water turbidity ranged from 0.04 ± 0.00 to 0.10 ± 0.00 NTU (Nephelometric turbidity units), the turbidity mean value still falls within the permissible limit of 5NTU of WHO standard. High turbid waters are often associated with the possibility of microbiological contamination, as high turbidity makes it difficult to disinfect water properly (DWAF, 1998 and Odjadjare and Okoh, 2010), which enables the water to be suitable for domestic use with reference to turbidity which was also supported by Garg *et al*., 2006.

Heavy Metal Concentration

The mean concentration values of heavy metals (Cr, Cd and Fe) in the water samples except Copper and Zinc were higher and these has exceeded the permissible limit set by WHO (2011) and NIS (2015), although essential to human life, copper can harm the liver and kidneys, induce stomach and intestinal discomfort, and cause anemia in excessive doses (Tepe, 2014). Zn is a naturally common element that is frequently found as a contaminant in food waste, agriculture, the production of insecticides, and the creation of antifouling paints (Badr *et al*., 2009) and it could pose a serious threat to both the environment and human health. Iron has the highest concentration among other metals with 35.660 ± 13.93 mg/l in sample LS, 10.764 ± 3.30 mg/l in MS and 2.001 ± 0.51 mg/l in US. Iron damages human tissues and contributes to a number of ailments when present in excessive concentrations. The mean concentration values obtained in Copper and Zinc were below the permissible limit of WHO (1993) and NIS (2015). This result is in agreement with the analysis conducted by Ruqia *et al., (*2015) where chromium, cadmium and iron concentration were above the permissible limit and also reported by Kamaruzzaman *et al*., 2011 and Mortuza and Al-Misned, 2017.

The FTIR of water hyacinth showed a strong peak at the range between 2356.62-1034.00. At 1447.59-1714.19 range,

its functional group showed C=C and C=O which is the carbonyl stretching vibrations, always strong and a single carbonyl group usually produces the strongest band in a spectrum. The peak shown at 1034.00 has C-O stretch in structures which contained carboxylic acids, ethers, ethers and alcohol as reported by Medhat *et al*., 2015, Medhat *et al*., 2009 and Munene *et al*., 2020. Water hyacinth has a well-shaped fibril with rigid lignin structure coated surface. Uddin and Nasir (2013) reported a firm and highly ordered structure in water hyacinth biomass using SEM. The EDX micrograph shows that Silicon has the highest percentage of 72.45% followed by Silver which has 9.55% and other elements. Water hyacinth as a bio-sorbent was efficient for the reduction of heavy metals (Fe, Cu, Zn, Cr and Cd) in the located samples (US, MS, LS) at varying concentration (0.001g, 0.005g, 0.010g) and contact time (24hrs, 48hrs, 72hrs).

Iron was greatly reduced in the effluent from LS when treated with water hyacinth from 35.660mg/l to 3.452mg/l at 0.005g during 24hrs. The lowest reduction efficiency of the bio-sorbent was recorded in the MS during 48hrs (8.426mg/l) for 0.010g of the bio-sorbent dose.

Copper was reduced in the water samples of US. The concentration of copper in the water sample of US when treated with the bio-sorbent reduced from 0.057mg/l to0.017mg/l at 0.010g during 48hrs. No reduction in the initial concentration of the metal ion was observed for all doses (0.001g, 0.005, 0.010g) of the bio-sorbent introduced to the sample US with varying contact time (24hrs, 48hrs, 72hrs). This could be as a result of the low initial concentration of copper metal ion in the sample. In MS the bio-sorbent dosage of 0.001g at varying contact time was efficient in the reduction of the metal.0.005g and 0.010g of the bio-sorbent was only efficient in the reduction of copper during 24hrs with the highest adsorption efficiency 0.037mg/l observed for 0.10g. No reduction was observed during 48hrs and 72hrs.

From the result, it could be deduced that the most effective contact time for the removal of copper in all the collected samples was during 24hrs and the most efficient bio-sorbent dosage for the reduction of copper is 0.001g. The highest adsorption efficiency in the removal of Zinc in the collected samples was observed in the sample LS with a decrease in its concentration from 2.852mg/l to 0.334mg/l using 0.001g of the bio-sorbent at 48hrs.

Chromium ions were successfully removed by water hyacinth in Asa River, most especially in MS and LS. At varying contact time (24hrs, 48hrs, 72hrs) and bio-sorbent dose (0.001g, 0.005g, 0.100g), the bio-sorbent was able to adsorb chromium metal ions completely hence facilitating its complete removal. In US, a reduction in the concentration of Chromium was noticed during 24hrs in different doses of the bio-sorbent. At 24hrs, the concentration of chromium reduced from 0.240mg/l to 0.089mg/l, 0.000mg/l and 0.084mg/l using 0.001g, 0.005g and 0.010g of the bio-sorbent respectively. During 48hrs and 72hrs, there was complete removal of the Chromium metal ions at all masses of the bio-sorbent (0.001g, 0.005g, 0.010g) according to Yao and Ramelow, 1997.

Water hyacinth was efficient in the removal of cadmium metal ions in all collected samples. At varying contact time (24hrs, 48hrs, 72hrs) and bio-sorbent dose (0.001g, 0.005g, 0.010g), the bio-sorbent was able to absorb cadmium metal ions completely hence facilitating its complete removal. This study is in agreement with the report gotten from Adewoye *et al.,* 2021 which established the efficiency of water hyacinth in the adsorption of heavy metals.

From the result, it was deduced that the WH, removes the metals (Cd and Cr) from the samples collected because the efficiency of the absorption properties was improved for its ionization of its various functional groups presented on the surface of the adsorption in aqueous solutions and the biomass was treated with acid and alkali as a result of their ability to engage in cation binding with the metal ion according to Elangovan *et al*., 2008 and Mahamadi and Nharingo, 2010.

5. Conclusion

This study focused on the impact of industrial discharges on Asa river located at Ilorin, Kwara State, Nigeria. The study however revealed the industries wastewater usages in the vicinity of considered river releasing their effluent into the river with excessive quantities of physical, chemical, and heavy metal components, exceeding the National Industrial Standards and World Health Organization's standards for these criteria and making the water not suitable for usage and by reducing these components to a minimal level to conform with the standard guideline for usage as domestic and other purposes. The majority of heavy metals is naturally carcinogenic and can cause serious problems for humans and the aquatic ecosystem. Thus, for the removal of these heavy metals from waters and rivers, water hyacinth (*Eichhorniacrassipes*) has proven to be efficient. The presence of high percentage of silicon in water hyacinth is responsible for the complete removal of cadmium in all water samples used. Iron being the most abundant metal in the water samples collected was greatly reduced but not totally removed, same goes for other metals (Cu, Zn) partially in Cd and totally in Cr. The concentration of copper from the heavy metal analysed for the samples was reduced and still falls within the standard permissible limit for NIS (2015) and WHO (1993). Therefore, it could be recommended that industries around the vicinity should adopt the use of water hyacinth for treating their wastewater in order to achieve the highest adsorption efficiency and further studies should be conducted by increasing the adsorption time for complete removal of metals not totally adsorb under this study.

References

[1] Ademoroti, C. M. A. (2001). "Studies on physicochemical methods of wastewater treatment" Ph. D. Thesis, University of London.59-84.
[2] Adewoye, S. O., Adenigba, V. O., and Adewoye, A. O. (2021). Phycoremediation of Heavy Metals from a point source in Asa drainage systems using water hyacinth.4th international conference in science and sustainable development.

[3] Ahaneku, I. E., and Animasahun, I. M. (2013). Determination of water quality index of river Asa, Ilorin. Nigeria. *Advance in Applied Science Research.4* (6) 277-284.

[4] Alexander Decker (2013). Analysis of physicochemical parameters of sewage water used for irrigation in Bauchi metropolis nigeria. *International peer-reviewed academic journals.*

[5] APHA (1998). Standard method for Examination of water and waste water, 20th edition. American Public Health Association, Washington D. C.

[6] Arimoro, F. O., Iwegbue, C. M. A and Enemudo, B. O (2008). Effects of cassava effluent on benthic macroinvertebrate assemblages in a tropical stream in southern Nigeria. Zoological Lituanica., **18**: 2-12

[7] Ashok, L., Dong, H., and Triberi, S (2006). Environmental Monitoring and Assessment.1**13**: 411-429.

[8] Azrina, A., Khoo, H. E., Idris, M. A., Amin, I and Razman, M. R (2011). Major inorganic elements in tap water samples in Peninsular Malaysia. Malaysian journal of Nutrition.1**7** (2): 271-276.

[9] Badr, N. B. E., El-fik, A. A., Mostafa, A. R., and Al-mur, B. A (2009). Metal pollution records in core sediments of some Red sea coastal areas, kingdom of Saudi Arabia. Environmental monitorind Association.1**55**: 509-526.

[10] Bello, O. S., Lasisi, B. M., Adigun, O. J., and Ephraim, V. (2017). Scavenging Rhodamine B dye using *moringaoleifera* seed pod. *Journal of chemical speciation and Bioavailability.2**9*** (1) 120-134.

[11] Dagne, B. B. (2020). Determination of Heavy metals in wastewater and their Toxicological implications around Eastern industrial Zone, CentalEthopia. Journal of Environmental chemistry and Ecotoxicology.1**2** (2) 72-79.

[12] Dalal, L. P., Kalbende, S. P., and Nisal, R. S. (2013). Physico-chemical Assessment of Water Quality of River and the Hydro-biological Study of Algae. *International Journal of Scientific & Engineering Research.4* (3) 2229-5518.

[13] DWAF, (1998). *Qualityof Domestic Water Supplies. Assessment Guide.1 (2nd. Ed.)* Department of Water Affairs and Forestry, Department of Health and Water Research Commission.

[14] Elangovan, R., Philip, L., and Chandraraj, K (2008). Biosorption ofchromium species by aquatic weeds: kinetics and mechanism studies. *Journal of Hazardous Materials*.1**52**: 100-112.

[15] FEPA (Federal Environmental Protection Agency) (1991). Guidelines to Standards for EnvironmentalPollution Control in Nigeria, FG Press Lagos Nigeria.238

[16] Garg, R. K., Saksena, D. N., and Rao, R. J (2006). Assessment of physicochemical water quality of Harsi Reservoir, District, Gwalior, Madhya Pradesh. *Journal of ecophysiology and occupational health*.6: 33-40.

[17] Heydari, M. M., and Bidgoli, H. N (2012). Chemical analysis of drinking water of Kashan District, Central Iran,. *WorldAppliedSciencesJournal*.16 (6): 799-805.

[18] Juan, C. M., and Lilian, G. (2012). Heavy metals ions adsorption from wastewater using activated carbon from orange peels. *E-Journal of chemistry.9* (2) 926-937.

[19] Kamaruzzaman., B. Y., Shuhada, N. T., Zahir, M. S., Akbar, S. S., Jalal, K. C. A., Al-Barwani, S. M., and Goddard, J. S (2011). Contamination of lead, copper and Zinc in the bottom sediment of Tuba Island waters of Langkawi, Malaysia. *Journal of chemistry***27** (2): 505-510.

[20] Katsoyiannis, I. A., and Zouboulis, A. I (2013). Removal of Uranium from contaminated drinking water a mini review of available treatment methods, desalination and water treatment.5**1** (13-15): 2915-2925.

[21] Kavcar, P., Sofuoglu, A., and Sofuoglu, S. C (2009). A health risk assessment for exposure to trace metals via drinking water ingestion pathway. *International Journal of Hygiene and Environmental Health*.2**12** (2): 216-227.

[22] Khan, S., Shahnaz, M., Jehan, N., Rehman, S., Shah, M. T., and Din, I (2013). Drinking water quality and human health risk in Charsadda District, Pakistan. *Journal of Cleaner Production*.6**0**: 93-101.

[23] Kesalkar, V. P., Khedikar, I. P., and Sudame, A. M. (2012). Physico-chemical characteristics of wastewater from Paper Industry. *International Journal of Engineering Research and Applications (IJERA).2* (4) 137-143.

[24] Mahamadi, C., andNharingo, T (2010). Competitive adsorption of Pb (II), Cd (II) and Zn (II) ions onto *EichhorniaCrassipes*in Binary andTernary systems. *Bioresource. Technol., **101*** (3): 859-864.

[25] Medhat, I., Oliver, K., and Traugott, S. (2009). Molecular Spectroscopic study of water hyacinth dry matter. *The open chemical physics journal*.2**,** 1-6.

[26] Medhat, I., Osama, O., Abdel, A M., and Hanan, E. (2015). Spectroscopic analysis of water hyacinth: FTIR and modeling approaches. *Der pharmachemical journal*.7 (9) 182-188.

[27] Medudhula, Thirupathaiah, Samatha., and ChinthaSammaiah. (2012). Analysis of water quality using physicochemical parameters in lower manair reservoir of Karimnagar district, Andhra Pradesh. . *International journal of environmental sciences,* **3** (1) 172-179.

[28] Mohamad, H. H. A and Amaal, M. A (2017). Removal of some heavy metals from aqueous solutions using natural wastes orange peel activated carbon. *IJRDO-JournalofAppliedScience*.3 (4): 13-30.

[29] Morris, R. L. (2005). "Determination of iron in water in the presence of heavy metals"; *Journal of Analytical chemistry.2**5***, 1376-1382.

[30] Munene, J. M., Onyatta, J. O., and Yusuf, A. O. (2020). Characterization of water hyacinth powder using FTIR Spectroscopy and the Adsorption behavior of Pb^{2+}, Cd^{2+}, Zn^{2+}, Ni^{2+}, and Cr^{2+} in aqueous solution. *Asian journal of Applied chemistry research.6* (1): 47-55

[31] Ndimele, O., and Kumolu, J (2012). Some aspects of the physicochemistry and heavy metals content of water, sediment and cynothrissamento (Regan, 1917) from Badagry creek, Lagos. Nigeria. *Tre. AppliedScienceResources*.7: 724-736.

[32] Nigerian industrial standard (NIS) (2015). Nigerian standard for drinking water quality.554

[33] Odjadjare, E. O., and Okoh, A. I (2010). Physicochemical quality of an urban municipal wastewater effluent on the receiving environment. *Journal of Environmental Monitoring Assessment.1*70: 383-394.

[34] Olakunle, M. O., Inyinbor, A. A., Dada, A. O., and Bello, S. O. (2017). Combating dye pollution using cocoa pod husks: a sustainable approach. *International journal of sustainable Engineering.*

[35] Olorunfemi, O and Gabriel, O. M (2018). Physico chemical properties and heavy metals concentration in waste water discharged from two industries in Agbara, Lagos State, Nigeria. *International Journal of Public and Environmental Health.3*, 32-37Ogidiaka, E., Esenwo, I. K., and Ugwumba, A. A. A (2012). Physicochemical parameters and benthic macroinvertebrates of Ogunpariver at Bodija, Ibadan. *Journal of Environmental.*8**5** (1): 89-97.

[36] Ogundiran, M. A., and Fawole, O. O. (2014). Assessment of the impact of industrial effluent discharged on the water quality of Asariver, Ilorin, Nigeria. *Journal of Environmental Science, Toxicology and Food Technology.8*, 80-98.

[37] Ogunwemimo, C. A., and Osuala, I. A (2004). Physicochemical parameters and macrobenthos of an estuarine creek and an artificial pond in Lagos, Southwestern. Nigeria.1 (2) 128-132

[38] Ogunleye, I. O., and Izuagie, A. A. (2013). Determination of heavy metal content in some industrial effluents from Ondo State, Nigeria, *Journal of Environmental Chemistry and Ecotoxicology.*1**0**, 216-219.

[39] Rahmannian, N., Siti, H. B. A., Homayoonfard, M., Ali, N. J., Rehan, M., Sadef, Y., and Nizami, A. S (2015). Analysis of physicochemical parameters to evaluate the drinking water quality in the state of Perak, Malaysia. *Journal of chemistry.6*5-75.

[40] Ruqia, N. M. K., Muhammad, M., Hameed, U. R., Naveed, U. R., Surrya, S., Nosheen, A., Muhammad, S., Mohib, U., Muhammad, R., and Zeenat, S (2015). Accumulation of Heavy Metals (Ni, Cu, Cd, Cr, Pb, Zn, Fe) inthe soil, water and plants and analysis of physico-chemical parameters of soil and water Collected from Tanda Dam kohat. . *Journal of Pharmaceutical Science and Resources.7* (3): 89-97

[41] Scatena, F. N (2000). Drinking water quality, Drinking water from forests and grasslands: Asynthesis of the scientific literature. General Technical Report SRS-39. Department of Agriculture, Southern Research Station, Asheville, NC, USA.

[42] Sharma, A., Mudgal, I. K., Sharma, A., and Sharma, S (2004). Fish diversity of Yashwatsagai reservoir indore. *Journal of Environmental Zoology.1*8 (2): 117-119.

[43] Shankhadarwar, S. D (2015). Heavy metals and Physicochemical properties of Soils and water from Sewage treatment plant. *Journal of Chemical and Pharmaceutical Research.7* (10): 626-629.

[44] Simpi, B., Hiremath, S. M., Murthy, K. N. S., Chandrashakarappa, K. N., Patel, A. N., and Puttiah, E. T (2011). Analysis of water quality using physicochemical parameters of Hosali tank in Shaimaga district, Karmataka, India. *Global Journal of Science Resources.1*1 (3): 4-5

[45] Taylor, E. W. (2000). "Examination of wastes and water supplies (7th ed.); Little Brown &Co., Boston.

[46] Tekade, P. V., Mohabansi, N. P., and Patil, V. B. (2011). Study of physicochemical properties of effluents from soap industry in Wardha. http://www.rasayanjournal. com.4 (2) 461-465 ISSN: 0974-1496 CODEN: RJCABP.

[47] Tepe, O., and Boyd, E (2002). Nitrogen fertilization of golden shiner ponds. Norway Amr. Aquaculture.6**4** (4): 284-289.

[48] Tepe, O (2014). Toxic metals: Trace metals-chromium, Nickel, Copper and Aluminium, In Ecyclopedia of food safety, edited by Yasminemotarjemi, Academic Press, Waltham.356-362.

[49] Uddin, M. D., and Nasir, E (2013). Adsorptive removal of methylene bluefrom aqueous solutions by means of HCl treated water hyacinth: isotherms and performance studies. *Journal of Pure Utilization Reaction Environment.2* (3): 63-84.

[50] Venkatesharaju, K., Ravikumar, P., Somaskekar, R. K., and Prakash, K. L (2010). Physicochemical and Bacteriological investigation on the river Cauvery of Kollegal stretch in Karnataka. *Karnataka University Journal of Science Enginering Technology.6* (1): 50-59.

[51] Wetzel, R. G., and Likens, G. E (2006). Limnological analysis.3rd ed. Springer-Verlag, New York.391-340.

[52] World Health Organization (WHO) (2006). WHO Guidelines for the safe use of wastewater, excreta and greywater. Vol I: Policy and Regulatory Aspects, Vol. II: Wastewater use in Agriculture. Vol. III: Wastewater and excreta use in aquaculture. Vol. IV: Excreta and greywater use in agriculture. Geneva: World Health.

[53] World Health Organization (WHO) (2011). WHO Guidelines for drinking water.4th edition.

[54] Yao, H., and Ramelow, G. J (1997). Evaluation of treatment techniques forincreasing the uptake of metal ions from solution by nonlivingbiomass derived from several strains of lichen, Sphagnum (peat) moss, and *Eichhorniacrassipes* (water hyacinth) root. Microbios**90**: 97-109.