

**Kurdistan Regional Government  
Ministry of Higher education & Scientific Research  
University of Sulaimani  
College of Agricultural Engineering Sciences**



# **APPLICATION OF SORGHUM AND AQUATIC MICRO/MACROPHYTES TO IMPROVE WATER QUALITY OF THE POLLUTED TANJARO RIVER FOR IRRIGATION IN SULAYMANIYAH, KRI**

**A Dissertation**

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(Environmental Pollution)**

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# بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

*In the name of Allah/God, the Most  
Gracious, the Most Merciful*

أَوَلَمْ يَرَ الَّذِينَ كَفَرُوا أَنَّ السَّمَاوَاتِ وَالْأَرْضَ كَانَتَا رَتْقًا  
فَفَتَقْنَاهُمَا<sup>ط</sup> وَجَعَلْنَا مِنَ الْمَاءِ كُلَّ شَيْءٍ حَيٍّ<sup>ط</sup> أَفَلَا  
يُؤْمِنُونَ {٢١:٣٠}

*Have those who disbelieved not  
considered that the heavens and  
the earth were a joined entity, and  
We separated them and made from  
water every living thing? Then  
will they not believe? {21:30}*

## **Supervisor Certification**

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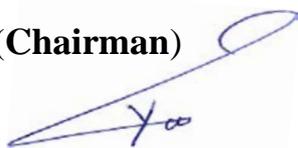


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DEDICATION

DEDICATED TO.....

ALL CREATURE.....

MY LEAFS (SIMA AND SAN)

PART OF MY LIFE (SAMAN)

MY DEAR FATHER AND MOTHER

MY SWEET BROTHER AND SISTER.....

ZHINO

2020

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## SUMMAR

Phytotechnology was applied to assess the capacity of microphytes (algae) and macrophytes (duckweed) to remediate pollutant from Tanjaro River water based on irrigation standards. The results showed clear differences between the untreated and treated polluted Tanjaro River water samples. Untreated and treated water sample were analyses for some physiochemical measurements include; temperature, pH, dissolved oxygen, biological oxygen demand, total dissolved salts, electrical conductivity, turbidity and Chlorophyll *a*,  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{Cl}^-$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ , Fe, Co, Cd, Pb, Cr, Cu, As, Zn and Mn. Fifty liter of water sample from Tanjaro River water treated by open pond ex-situ system of algae and duckweed, declines in those values, except for dissolved oxygen and Chlorophyll *a*. Nutrient removing efficiencies of the algae and duckweed indicate the ability to remove 100% of the Fe, Cd, Pb, Cr and As in the studied water sample, although algae showed a higher efficiency to remove Co, Cu, Zn and Mn in comparison with duckweed; duckweed showed efficiency to remove  $\text{PO}_4^{3-}$ ,  $\text{Cl}^-$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ . The calculated value of irrigation water quality index (IWQI) is 12 of the untreated water (low suitability for irrigation) improved after treatment with algae and duckweed to 13 and 14, respectively. Irrigation water quality index (IWQI) improved the suitability for irrigation 8 and 17 % by duckweed and algae, respectively.

The results of irrigation water sampling from the polluted Tanjaro River that used for irrigation frequency, during the special sorghum soil pot experiment (August 1, 2018 to October 1, 2018) concluded the water sampling from the Tanjaro River water showed variation in values of all the measurements and water quality index during the irrigation period in (August 1, 2018 to October 1, 2018), this variation is due to the sewage composition from Sulaymaniyah city.

The results of the sorghum soil pot experiment and irrigation frequency (1-time/week, 2-times/week, and 3-times/week) of soil showed a significant difference between irrigation frequency and their effects on soil chemistry. There are positive increases in ratio of metals and nutrients discharging from soil pots during the sorghum experiment. The results showed that irrigation frequency have an effect on the levels of the following metals (Fe, Co, Cd, Pb, Cr, As, Cu, Zn and Mn)  $\text{mg L}^{-1}$  discharging through the soil during the time. Also, using the long-term of polluted water from Tanjaro River for irrigation affects the groundwater. However, the results of cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$  and  $\text{Na}^+$   $\text{mg L}^{-1}$ ) and anions ( $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$  and  $\text{SO}_4^{2-}$ ) that are concentrated in the discharged water showed that the irrigation frequencies have a positive effect on the cations and anions discharging from soil especially by using the Tanjaro River for irrigation. The results indicated that the ions can reach ground-water through the soil by repeating the polluted water in the long-term of irrigation. These results confirmed that by

increasing the irrigation period the values of (DO, pH, EC, TDS, and T) decrease in the discharged water from the soil, except turbidity, as it increases and this result was expected given the soil mechanisms working as a filter.

The results of polluted water irrigation effects on the soil chemistry showed a negative relation between irrigation frequency and total heavy metals with non-significant differences between times of irrigation during 2 months of the experiment, except Pb which shows a significant difference with irrigation frequency. The heavy metals' total concentration was decreased in the soil during the experiment, as they are up taken by sorghum and discharged from the soil. Also, the cations ( $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) showed similar trends in the soil where the concentration decreased in the soil during the experiment and the irrigation frequency showed non-significant differences for  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations. On the other hand,  $\text{K}^+$  and  $\text{Na}^+$  showed effects by irrigation frequency, where in the 1 and 2-time irrigation/week, the concentration increased in the soil and the 3-time irrigation/week decreased. Results of total P concentration affected by irrigation frequency was increased in the soil under 1 and 2-time irrigation/week and decreased under 3-time irrigation/weeks. Total percentage of nitrogen decreased in the soil, the total percentage of carbon increased in the soil during sorghum pots experiment, and there was a significant difference between irrigation frequency for both (% Nitrogen and % Carbon).

Sorghum has the ability to uptake metals and nutrients in their roots more than in their shoot system, except  $\text{K}^+$ , N, and C as they were observed in higher concentrations in the sorghum shoots. Also, there were significant differences between irrigation frequency in metals and nutrient concentrations in the roots except for Cd, Pb, Cu and K as no significant differences were observed for them. On the other hand, the concentrations of metals and nutrients in the shoots showed low significant differences between irrigation frequencies during the experiment.

The results of increased of metal percentage in the soil after use the Tanjaro River water for irrigation during the sorghum soil pot experiment was also observed in the soil without sorghum (control). The order of the increase was  $\text{Mn} > \text{As} > \text{Cu} > \text{Cd} > \text{Cr} > \text{Pb}$  except for Fe, Co and Zn in comparison with the metal content in the initial soil, in conclusion when the soil is irrigated by polluted water from the Tanjaro River the metals accumulated in the soil.

The decision about (algae, duckweed) ability for metals remediation was evaluated by the biological accumulation coefficient (BAC) these results showed that algae are able to phycoremediate metals Fe, Mn, Cu, Cr, Co and Zn. Duckweed has the ability to phytoremediate metals Fe, Cu, Mn, Cr, Co and Zn. Sorghum can phytoremediate metals Fe, Co, Cr, Pb, Cu, As, Zn and Mn except Cd where  $\text{BAC} > 1$ , and translocate the metals Co, Cr, As, Cu, Zn and

Mn to the shoots of sorghum, cannot translocate and accumulate Fe, Cd, and Pb in their shoot system, on the other hand have ability to phytostabilization of metals (Fe, Co, Cr, Cd, Pb, As, Cu, Zn, and Mn). Algae, duckweed, and sorghum cannot accumulate the metals Pb and Cd since the BAC <1, the duckweed showed capacity for heavy metals extraction more than algae and sorghum.

The results of present study showed that algae and duckweed can be used in bioremediation for the Tamar River water before using the water body as a source of irrigation. In addition, direct use of polluted water as an irrigation source for those types of plant cannot be used as daily sources for human consumptions. However, potentially using the Tamar River water for irrigation has harmful effects on soil, plants and ground-water. This requires annual research and monitoring in the future. These findings show the potential of phytotechnology for environmental remediation in an agriculturally important region of Iraq.

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# CHAPTER ONE

## INTRODUCTION

The present study exploring to remediation the polluted water from Tanjaro River by wastewater of the Sulaymaniyah City, using aquatic microphytes, macrophytes and plants to degrade, extract, contain, or immobilize pollutant from Tanjaro River water. Although heavy metal removal mechanisms phycoremediation and phytoremediation are relatively new biotechnologies that have received attention lately as innovative, cost-effective alternatives to these more established treatment methods. These two methods (open pond-situ algae and duckweed and sorghum soil pot) have been successfully used to eliminate hazardous heavy metals and other harmful pollutant in the Tanjaro River. Although plants are commonly used in phytoremediation to remove and degrade environmental pollutants (Chekron, 2013), many living organisms can accumulate certain toxic at body concentrations much higher than present in their environments (Kord *et al.*, 2010). An example is algae, which can bioaccumulate and remove heavy metals (both free and complexed with organic matter) from the environment. Microalgae removes heavy metals directly from polluted water by two major mechanisms: first, metabolism dependent uptake into their cells at low concentrations and second, biosorption, which is a non-active adsorption process cause to accumulation of metals from polluted water (Matagi *et al.*,1998).

The groundwater-fed Tanjaro River is polluted by heavy metals from urban and suburban sewage discharge areas from the City of Sulaymaniyah and is ultimately, used as a source for agricultural irrigation (Muhammed, 2002 and Majid *et al.*, 2018) Soil properties such as the availability of nutrient concentrations, organic carbon content, microbial biomass, C, N, and P concentrations, enzymatic activity, and heavy metal concentrations will likely be affected by the irrigation of this polluted water. Indeed, the concentration of heavy metals in plants was several-fold higher in roots and shoots at polluted water-irrigated sites in comparison with soil irrigated by unpolluted water (Bomposem *et al.*, 2012).

Polluted surface water from Tanjaro River using for irrigation has been reported to lead to certain beneficial changes in physiochemical and biological properties of the soil such as increased CEC and water holding capacity, but can increase the concentrations of heavy metals to contaminant levels (Hamdy,1992; Singh and Agarwal, 2012). The intermittent use of clean water in such areas, may reduce this metal contamination in the plants and maintain soil fertility.

The soil in agricultural production irrigated by the Tanjaro River polluted by heavy metals were present in the Sulaymaniyah wastewater (Muhammed, 2002).

Long-term irrigation of soil by polluted water from Tanjaro River has been reported to change chemical, physical, and biological properties of soil (Wana; Okieimen, 2011). Through contaminated soils, heavy metals originating from the Tanjaro River can enter the food chain of animals and humans. This process is a potential health hazard and has negative effects with respect to various heavy metals on human health (Gottlieb *et al.*, 2010). In addition to these hazards, biological contamination of the Tanjaro River also poses serious environmental and human-health hazards (Rashid, 2010).

Plants (macrophytes) irrigated by Tanjaro River water have been shown to accumulate heavy metals in root and shoot parts as well as bringing that polluted water closer to irrigation water quality standards (Ganjo, 2001 and Khwakaram, 2009). Although Khwakaram (2009) studies showed the potential of plant bioremediation of wastewater before mixing with Tanjaro River water, they did not emphasize the bioremediation capacity of microphytes (algae) nor compare it with macrophytes (duckweed). Our study aims to use algae and duckweed in the phytoremediation of Tanjaro River water. Algae and duckweed grow naturally in the Tanjaro River especially in the summer season under high sewer discharge from the Sulaymaniyah city.

This study aims to use open pond ex-situ algae, duckweed, and sorghum soil pot experiment in the phyco/phytoremediation of Tanjaro River water. In addition, this study examines the impact of the micro/macrophytes and plants on surface polluted water and soil due to the uptake of nutrients and metals from the soil solution and Tanjaro River water.

The proposed objectives of this study are:

1. Test the ability of biotechnology—specifically, micro/macrophyte accumulation of metals—to remediate Tanjaro River water to meet international irrigation standards.
2. Evaluate the effect of polluted water irrigation frequency on heavy metal contamination in soils phytoremediated with sorghum plant.

## **CHAPTER TWO**

### **LITERATURE REVIEW**

#### **2. Biological Treatment Technology**

phytotechnology term used for cleaning the environment pollutant by plant or organisms where they have photosynthesis system can be used in the bioremediation processes (Sharma, 2008). In addition, there are abundant bioremediate in nature that can be applied and use as a bioremediation agent against a broad range of pollutants. In general, the agent used for bioremediation included Bactria, fungi and macro/microalgae (Davis *et al.*, 2000; IYE 2015).

#### **2.1 Bioremediation**

Bioremediation is a branch of biotechnology science that use microorganism to clean up environmental contamination (air, water, and soil) (Fiorenza *et al.*, 1991). Biological materials have been used to reduce the hazards of heavy metal concentration in the environment (Boopathy, 2000; Ganjo and Ahmmmed, 2010; Dzionek, 2016). So, bioremediation can be defined as using biological processes and living organisms to destroy the organic and chemical contaminants. In other words, it is restoration of the damaged environment by using part of nature, which is biology (Kumar *et al.*, 2015). Sasikumar and Papinazath (2003) applied the new term on biotechnology which is called renewable energy where bioremediation technology took place to bio-transform the pollutant material into harmless products and renewable source or another form of energy. bioremediation can protect the life cycle and prevent the transformation of hazards toxic metals and risky contaminants from an ecosystem to another (Iye, 2015).

Bioremediation is consider a cost-effective solution to reduce the variety of environmental pollution by using natural and biological processes to clean the pollutant site (Ganjo 2001; Vidali, 2001 and Verma and Suthar, 2015). In addition, IYE (2015) investigated that the bioremediation reduced the level of a toxicant to the level of lower than the limit proposed by regulation agencies. The application of bioremediation is a sustainable process that can be applied for all environmental components that have a tendency towards (e.g. soil, water and air) thereby, increases the sustainability of the environment and the quality of life in that specific biota (Goltapeh *et al.*, 2013).

## 2.1.1 Type of bioremediation

### 2.1.1.1 *In-situ* (On-site)

These types of bioremediation were done *in-situ* in the pollution site without taking any engineering steps to enhance process. *In-situ* bioremediation is considered the most desirable due to its cost-effectiveness and fewer site disturbances, the amount of by-product of remediation was less and remediate the environment problems immediately (Chaudhary and Sharma, 2014 & Chaudhary and Sharma, 2014). Furthermore, the depth of the polluted site may also restrict treatment effectiveness (Verma and Suthar, 2015). *In-situ* bioremediation also has some disadvantages including it is time-consuming, a seasonal variation where can not be controlled, the weather condition might have a direct impact on the microbial activity and at the end of remediation microorganisms will die because of decreasing the waste material. In such cases, it is recommended to use genetically engineered microorganisms (Adams *et al.*, 2017; Vidali, 2001 & Chaudhary and Sharma, 2014).

### 2.1.1.2 *Ex situ*

The bioremediation process here takes place somewhere outside the pollution site and therefore involves the transfer of contaminated soil or groundwater pumped to the bioremediation site, also surface water can be treated by *ex-situ* process (Vidali, 2001). According to Gavrilescu (2010) the disadvantages such as extra cost and risk related with the possibility of distribution of the contamination during transport, also more costly to handle due to excavation (Dzionic, 2016; Adams *et al.*, 2017). However, the advantage of *ex situ* bioremediation is that it is the more efficient removal of pollutants, during the controlling of physic-chemical parameters and minimum time of reclamation is needed. According to the phase of contaminations the *ex-situ* bioremediation divided into two systems; solid phase (including land treatment and soil piles) and slurry phase (including solid-liquid suspensions in bioreactors).

## 2.2 Phytotechnology

Phytotechnology is the use of biotechnology plants to mitigate environmental pollutant (Evans and Furlong, 2003). Recently, the conventional phytoremediation concept has been replaced by the word "phytotechnologies," used to describe all applications where plants are used to manage and control pollutants, even without eliminating or damaging them (ITRC, 2001). However, phytotechnology involves all types of living organisms that had the photosynthesis process and they would convert CO<sub>2</sub> to oxygen through using the sunlight and other nutrients in the medium to complete the photosynthesis processes. Goltapeh *et al.* (2013); IYE (2015) cited that the

macro and microphytes were part of the phytotechnology, although the byproduct of the plants or organisms can be spent in another technology and application, such as Biofertilizer composting, biodiesel and biofuel when tested for ability. ITRC (2001) have been identified a series of six Phyto technology mechanisms that can remove the various pollutants in different substrates; 1. phytotransformation, perfect for organic contaminants 2. rhizosphere bioremediation, applied to organic contaminants in soil 3. phytostabilisation, for organic and inorganic contaminants in soil 4. phytoextraction, useful for inorganic contaminants in all substrates 5. phytovolatilisation, which concerns volatile substances 6. evapotranspiration, to control hydraulic flow in the contaminated environment (Marmioli *et al.*, 2006).

### 2.2.1 Algae Bioremediation

Algae represent various groups of organisms, which have the capability to grow under different conditions. Algae can grow in both conditions high and low temperature, pH and salt concentration and also able to live in the water body and desert crusts or in symbiosis on the other living organisms (Skjanes *et al.*, 2013). The algae are thallophytes (plants lacking: leaves, stems, and roots) that have chlorophyll *a* as their primary photosynthetic pigment. On the other hand, the blue-green algae in evolution were closer to the bacteria than to the algae (Lee, 2008). The term phycoremediation apply on the process was to use the algae for remediation of pollutants, the algae have the capability to remove both (organic and inorganic) pollutant (Gusain and Suan, 2018).

Algae bioremediation, cleanup of wastewater by algae was studied 40 years ago (Cheng, 2014). The previous research study was devoted 220 growth of algae bio sorbent for remediation of heavy metals in the wastewater (Cheng, 2014). It is understood that the use of algae in environmental clean-up is more environmentally friendly and safe because it does not generate or produce additional toxins (Pittman *et al.*, 2011) ; (IYE, 2015).

Barsanti and Gualtieri (2006); Lee (2008) have categorized the algae-based on cell size into two groups; macro and micro algae (macro and micro phyta). Macroalgae (macrophyta) was introduced under the name of seaweed, can be seen without using the microscope macro algae multicellular contain numbers of cells, they have the (holdfast, tips and blades) look like (root, stem and leaves) in the higher plant (Lee, 2008). On the other hand, Micro algae are unicellular organisms were called the phytoplankton. They are small that cannot be seen without a microscope and have different colors such as, blue-green, green, red, and brown (Lee, 2008). According to Barsanti and Gualtieri (2006), both types of algae are important for biotechnology and bioremediation, especially for water treatment, also they are part of biotechnology of cosmetics, biofertilizer, supplement and biofuel. IYE (2015) notes that algae are considered to

have very high carbon capture and photosynthetic efficiencies compared to terrestrial plants and are categorized as either marine or freshwater plants. In addition, algae have economic benefits and more importantly for environment balancing and ecosystem improvement.

Bai et al. (2017) established that algae have an important role in carbon dioxide balancing on the earth, by photosynthesis processes algae exudate a large amount of oxygen and reduce the carbon dioxide in the environment, also protecting the environment from thermal pollution. Furthermore, algae use as the source of metal and nutrient like the supplement which may include to the medicine, algae pigment use for food color, however some part of algae cell use in the food industry in the Asian country consuming the algae as the sources of daily food (Abdel-Raouf, 2012).

Slade and Bauen (2013) noted that the wastewater treatment by algae biomass; algae up taking the macro nutrient and heavy metals in the wastewater by absorption and accumulation in the cell, also have the ability to destroy the organic compounds in the pollutant water through the biotransformation processes, algae biomass going over the technology of biofertilizer and biofuel. For there more algae including to the biogeochemical cycling of nutrients in the environment especially profitable in the cycle of; phosphorous, sulfate, silicon, nitrogen, and oxygen /carbon (Barsanti and Gualtieri, 2006).

### **2.2.1.1 Algae division**

Algae division is the most complex category and based on flagella, cell wall composition, pigment, food storage nature and cell organization( shape and colony formation), some species were introduced under name of bacteria like Cyanobacteria (Cyanophyta / blue-green algae) or sometimes include under the class of Chlorophyta but in general, they have some classes under each division (Barsanti and Gualtieri, 2006). Encyclopedia (2019) divided the algae into the six main divisions; Chlorophyta, phaeophyta, Crysophyta, Rodophyta, Pyrrophyta (Dinoflagellata) and Division of Eglenophyta.

### **2.2.1.2 Algae growth condition**

The Growth conditions of algae need to study the parameter was to have an effect on algae growth (Miao and Wu, 2004; Xu *et al.*, 2006; Li *et al.*, 2019). If one of the factors changed then the whole process affect especially on algal productivity and treatment efficiency. The growth rate of the algae depends on the several conditions such as (chemical; nutrient in the media carbon dioxide, physical; the light was most important for photosynthesis processes, temperature; and biological; the virus infections and competition between species). However, the operational factors such as dilution rate, mixing, harvesting frequency depth, and addition of bicarbonate affect the growth of microalgae (Rathod, 2016).

### **Light**

The light is one of the most important parameters for algae growth rate and it has a direct impact on photosynthesis of microalgae. Algae convert the light to heat and chemical energy through photosynthesis processes and 90% of the light energy is dissipated as heat only converts %10 of it to the chemical energy (Agarwal *et al.*, 2019). Then some species of algae were living in the dark condition, and they can grow on the organic compound by taking the Carbon and energy from decomposing of the organic matter, however, microalgae needs a light/dark condition for productive photosynthesis.

Algae needs the light for chemical reaction to produce (ATP) Adenosine triphosphate (NADPH) Nicotinamide adenine dinucleotide phosphate-oxidase), also and dark condition for biochemical phase synthesize essential molecules for growth (Benjamas and Salwa, 2012).

### **Temperature**

Microalgae biomass growth needs the optimum temperature, while the microalgae tolerate temperature between 16 to 27 °C, according to Barsanti and Gualtieri (2006), this range was close to other microorganisms (the relation between temperature and growth rate of algae are positive relation except for the humid region. In addition, when increasing the temperature increases the algae growth, then the overheating in humid regions reduces the growth rate of algae.

Also, the algae have a variety of divisions considering temperature conditions in which some algae species has the capability to grow and has the best growth rate in the low temperature between (2 to 6 °C). The algae need temperature for a chemical reaction in the medium. However, the temperature has effects on the metal concentration in the media especially in the case of wastewater treatment for nitrogen reduces (Vona *et al.*, 2004).

### **pH**

pH is an important factor that affects the microalgae growth rate, Azov, (1982) investigated that the pH value increases during microalgae cultivation by photosynthetic of CO<sub>2</sub> assimilation, also through the absorption of nitrogen by microalgae pH value increases in the medium, from every nitrate ion when reduces to ammonia produces one OH<sup>-</sup> ion (Rathod, 2016). Although this increasing of pH value causes the precipitation of phosphate, then the incident was CO<sub>2</sub> assimilation happen. Gassan *et al.*, (2009) reported that the highest growth rate of micro algae in the wastewater treatment ranges between 0 and 7. In general, the most algal species were cultured in pH value between 7 and 9, but the optimum pH value ranged between 8.2 to 8.7 (Chalivendra, 2014).

### **Salinity**

The condition of salinity for best microalgae growth is between 20-24 g/l, and the salinity should be lower than the native habitat of microalgae composition of lipid also the microalgae have a responsibility to the salinity. Furthermore, the increase of salinity was increased of the lipid content of algae cell, in addition all species of algae have the responsibility to salinity, also a positive correlation was seen between the (hexadecenoic acid and unsaturated fatty acid) and salinity, nonetheless, the unsaturated fatty acid percentage will increase when the concentration of NaCl is high (Fakhry and Maghraby, 2015).

Bartley *et al.*, (2013) showed that the photosynthetic activity was observed under the stress of salinity, they recorded decreasing of photosynthesis processes.

### **Nitrogen and phosphorus**

Nitrogen and phosphorus were an important and essential nutrient for microalgae growth rate, both (N and P) were available in the form of (N;  $\text{NH}_4^+$ ,  $\text{NO}_3$ ,  $\text{NO}_2$  and P; inorganic orthophosphate  $\text{PO}_4$ ) (Saikumar, 2014). Algae have availability for ammonium absorption especially uses the urea as a source of N. Then the mechanisms of N and P up taking by micro algae were depending on N:P ratio, if the ratio below the %30 the algae growth was determined by N limitation, when the ratio was more than %30 algae growth have limitation for P nutrient (Rhee, 1978).

#### **2.2.2 Duckweed bioremediation**

Aquatic macrophytes have the important role for improvement of water quality and remediation of wastewater, the mechanisms of water purification through the accumulation of heavy metals and other toxic nutrients, also most of them have a role of oxygen balancing in the water and environment.

The many species of the aquatic macrophytes were used for bioremediation of wastewater, because they have the ability to grow faster and easy to collect and cultivated (Skillicorn, 1993). According to Muradov *et al.* (2014) were pointed out the Duckweed (*Lemnaceae*) among those floating macrophytes. Duckweed has a diameter around 1 to 20 mm, and also has a high growth rate in comparison with the higher plant, when grown under ideal conditions such as; high levels of nitrates and phosphates, however at the cultivation period the surface area was covered by duckweed and can be doubled in less than 2 days (Muradov *et al.*, 2014).

Duckweed has the ability for bioremediation and accumulation of high level of heavy metals by producing the biomass, in addition, the duckweed species were used for recover the nutrient in the wastewater over 30 years ago ( Patel and Kanungo, 2010; Chaudhary and Sharma, 2014)

Furthermore, it was used as the source of protein and starch for animal feed, and in the application of bioethanol and composting (Muradov *et al.*, 2014). Duckweed also has potential as a natural water purifier, converting wastewater into pure water and edible Duckweed with little resulting sludge. The only drawbacks are that the plant requires a large surface area to grow (Gerber *et al.*, 2004).

### 2.2.2.1 Duckweed classification

Duckweed classify on four genera; *Spirodela*, *Wolffia*, *Lemna* and *Wolffiella*, belong those genera 37 species were identified in the world, however the three genera *Spirodela*, *Wolffia* and *Lemna* they have the most available species in the world.

In the family of Lemnaceae the *Lemna* is the largest genera group, this group is the most complexes group within the family, also the most abundant species is *lemna Gibba* (Scholz, 2019). Crawford *et al.*, 2006 mentioned the common spices of duckweed in the world; ***Lemna Species*** were divided into; *Lemna aequinoctialis*, *Lemna gibba*, *Lemna minor*, *Lemna minuta*, *Lemna obscura*, *Lemna perpusilla* and *Lemna trisulca*. ***Spirodela Species*** were divided into; *Spirodela polyrrhiza* and *Landoltia punctate*. ***Wolffia Species*** were contained; *Wolffia arrhiza*, *Wolffia borealis*, *Wolffia brasiliensis* and *Wolffia columbiana*. ***Wolffiella Species*** were divided into; *Wolffiella gladiate*, *Wolffiella lingulata* and *Wolffiella oblonga*.

### 2.2.2.2 Duckweed growth condition

Duckweeds are found in a wide variety of climatic zones and spread over the world except in the cold regions where the temperature is below 0 °C. During past years, duckweed species were found in the climates of tropical zones, however, duckweed was found rare in those regions was they have the gap between precipitation (high or low), they have faster growth rate in the warm and sunny conditions (Skillicorn *et al.*, 1993). Moreover, several environmental factors such as light intensity, salinity, temperature, pH, nutrient, capitation with other plant and toxin in the water can influence the distribution and growth rate of *Lemnaceae* species (Crawford *et al.*, 2006).

#### ***Temperature***

Duckweed growth rate depends on temperature and the optimum temperature for growth generally ranges between 17.5 to 30 °C, also the temperature effect may change depending on the duckweed species, some duckweed species can grow close to the freezing temperature below 17 °C (Oron, 1994), however, some species cannot grow when the temperature is above 35 °C.

Liu *et al.*, (2018) proved that growth rate is not only driven by temperature, as the light intensity has an important role in duckweed growth rate, the growth rate increase when the light increases.

### **pH**

Duckweeds can generally grow in the pH ranges between 5 to 9, although the best growth ranges between 3 and 10. And the tolerance pH limits were deference depending on the duckweed species (Caicedo *et al.*, 2000). In addition, the Duckweed biomass was doubling through 2 to 4 day in the pH range (6.5 to 7.5), also continuously ammonia is present and largely absorbed by duckweed. On the other hand, ammonia increases the pH in the solution, besides, which can be toxic and lost by volatilization (Porath and Pollock, 1982).

### **Conductivity**

Electrical conductivity has a positive effect on duckweed growth rate when the Ec between 0.40-0.50 dS/m duckweed show the maximum biomass, also the electrolyte conductivity (0.63 dS/m and 0.20-0.89 dS/m) respectively were supporting the high growth rate and biomass of duckweed (Khondker *et al.*, 1993).

### **Nitrogen, phosphorus and potassium**

In general, the duckweed growth rate controlled by sunlight and temperature more than the nutrient concentration, but the nutrient concentration is still important for biomass growth (Mkandawire, 2006).

Giblin *et al.* (2014) and Hasan and Chakrabarti (2009) investigated that duckweed absorbed the ammonia nitrogen (NH<sub>4</sub>-N) as a source of nitrogen; also duckweed tolerates concentrations of elemental N as high as 375 mg/l. After nitrogen, phosphorus and potassium are the essential nutrients for the rapid growth of duckweed. In addition, duckweed can uptake the p as a form of PO<sub>4</sub>-P concentration, also the good biomass growth of duckweed within the P concentrations is a value between 6 to 154 mg/l (Landolt, 1986; Mkandawire, 2006)

### **2.2.3 Sorghum bioremediation**

Sorghum, *Sorghum bicolor* (L), belongs to the grass family, there are many varieties of sorghum, the colors ranged (white, red and brown) (FAO, 1999). In the world generally it is the most consumed cereal for human food, when the sorghum use as bioremediation plant they lose the capacity for human food, also sorghum inside those plant have the potential for bioremediation, in addition of reducing the waste contamination, heavy metals in the water were used for the irrigation system. While sorghum is C4 crop with high biomass yield and known

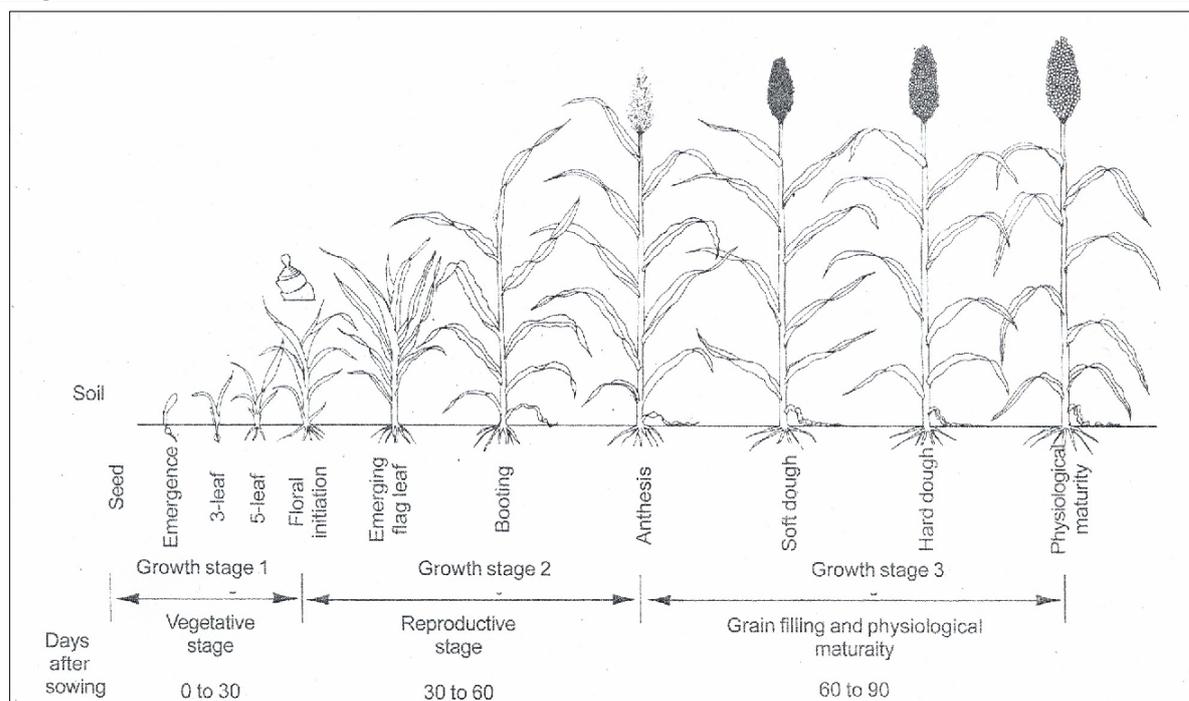
as the biotechnology plant used for biofuel in the most of country (Mashao and Prinsloo, 1994). Although sorghum mostly cultivated in the dry area in the shallow and clay soil (FAO, 1999), while when sorghum used for bioremediation purpose was accumulated the high level of contamination in their biomass, and unusable for livestock and food (Shafiei *et al.*, 2016).

### **2.2.3.1 Sorghum growth condition**

Sorghum plants one of those plant capabilities for adaptation in the drought condition and non-fertile condition, can also grow in the rainfall season and at a temperature between 20 to 30 °C, furthermore sorghum has three growth stages as shown in (Fig.2.1).

#### ***Temperature***

Sorghum crop can grow in the warm-weather, also it requires high temperatures for good germination and growth. The optimum temperature for its growth is (27 to 30 °C). Moreover the minimum temperature for germination is from 7 to 10 °C. However, the seed germination during the 10<sup>th</sup> to 12<sup>th</sup> day at 15 °C. On the other hand, the best time for planting is when the soil temperature is 15°C and sufficient amount of water is available in the soil in a depth of 10 cm (Mashao and Prinsloo, 1994).



**Figure 2.1 Sorghum growth stage (FAO, 1999)**

### *pH*

Sorghum is adaptive, it grows in highly alkaline soils to moderately acidic pH ranging from 6.0 to 6.5. While can grow in low fertility, but it is best adapted in the fertile and well drained soils (Clark, 2007; FAO, 2012; USDA, 2009).

### *Soil*

Sorghum is normally grown on heavy to medium clay soils. The most affecting factors enhancing the growth condition of sorghum yield is (soil structure, soil moisture and nutrient holding capacity). To protect the sorghum seed from diseases and insects one should encourage faster seeding to reduce the risk of seed germination, this protection usually depends on soil temperature, while to germinate in 7 days will need the 17 °C soil temperature, although at 15°C they will take around 12 days (Mashao and Prinsloo, 1994).

However, the soil moisture was another factor affecting seed germination, the seed should be sown at least in a 1 meter wet soil. Also, the soil fertility has an effect on the seed germination and growth rate of sorghum, the main nutrients required will be nitrogen, phosphorus, potassium, sulphur, and zinc (Serafin *et al.*, 2018).

### 2.3 Heavy metals in living organisms

Heavy metals are definite as metallic element with higher density and have toxicity at lower concentration. Heavy metals belong to the group of metal or metalloids with atomic density higher than 4 g cm<sup>-3</sup> or five times or more greater than water (Kumar *et al.*, 2015). However, in biochemistry heavy metals are defined as metallic elements with Lewis acid behavior, i.e., electron pair acceptor. About 53 chemical elements are considered as heavy metal, and most of these heavy metals are found as natural constituent of the earth crust and soil. From environmental perspective, any metals or metalloid that poses potential harmful effects to the living organism even at lower concentration can be termed as heavy metals. Most of these heavy metals (Zn, Cu, Mn, Ni, and Co) have vital function in plants, while other metals such as Cd, Pb, Hg, and Cr are found to cause toxic effects in biological system. The combined influence of urbanization, industrialization, and chemical consumption in agrarian practices has raised the heavy metal concentration up to the toxic level; hence its remediation is now considered as global concern. Heavy metals contamination in water is one of the most critical environmental problems, which include Cd, Cr, Cu, Hg, and Zn as common contaminants (Pathak *et al.*, 2019; Ahmad *et al.*, 2018; Kothari *et al.*, 2012).

Phycoremediation and phytoremediation is a potential tool to remove the excess toxics (heavy metal and organic contaminants) from the industrial waste stream. The algal duckweed and sorghum are eco-friendly work to remediated the contamination.

Therefore, algae have been documented as a sustainable and inexpensive vector for detoxification of noxious waste-loaded industrial waste stream. Algal species may bind up to 10% of their biomass as metals. Biosorption is the dominant mechanism in uptake of heavy metals either by active algal biomass or passive algal biomass and found as a cost-effective solution to eliminate heavy metals from industrial effluent (Praepilas and Pakawadee 2011). In case of passive algal biomass, biosorption doesn't involve in metabolic pathway; however, it entirely depends on interaction between the biomass and metal ion; hence it resembles with the binding of metal ions through ion-exchange resins. Contrary to the ion-exchange resins, biosorption involves various steps such as chelation, partial adsorption, complexation, micro-precipitation, etc. On the other hand, biosorption in active algal biomass is carried out through energy-mediated transport of metal ions through the cell membrane. The ability of metal sorption through various organisms has been widely reviewed by researchers and concluded that have massive potential to bind metal ions from very low concentration in the external solution (Kothari *et al.*, 2017; Ahmad *et al.*, 2017).

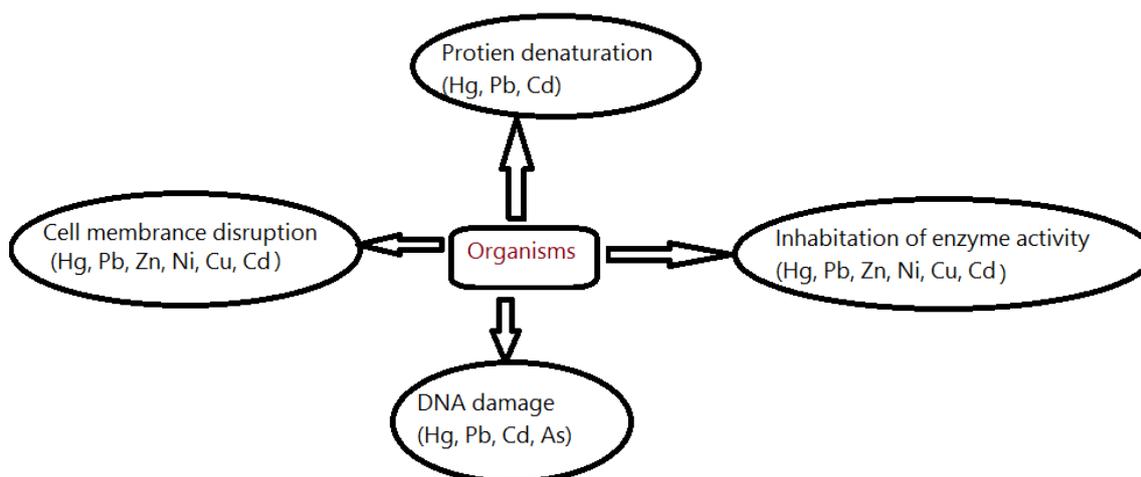
Duckweed also have interaction with heavy metals in the media and rolling as phytoremediator to accumulate the heavy metals, the proportion of metal uptake by duckweed was dependent on the metal concentration in the solution when only one kind of metal ion was present. It was decreased by increasing concentrations of other metals in mixtures of solutions. The metal uptake by the duckweed was always less than the loss of metal content in the relevant solution. This fact implied that the process of the uptake of metal ions by the duckweed may involve two stages. In the first, the metal is absorbed but then it is adsorbed by the duckweed (Robinson, 1988; Landesman et al., 2010).

Sorghum in those plant high ability to accumulate multiple metals in their shoots and roots without being affected by excessive metal contents, with high biomass production, metal accumulation ability and high tolerance against metal toxicity might have great potential in phytoremediation field (Yuan et al., 2019).

In addition, El-Meihy et al. (2019) summarized the ability of sorghum to enhance plant growth through the oxidative enzymes, photosynthetic pigments, growth characteristics, heavy metals uptake and heavy metals translocation.

### **2.3.1 Heavy metals up taking mechanisms by living cell**

Heavy metals do not participate in the metabolism of the body, but it is accumulated through different mechanisms which include bioaccumulation, bioconcentration, and biomagnifications illustrated in Fig (2.2) Organisms exposed in heavy metals tend to have protective mechanism against heavy metal toxicity. The HM concentration beyond a threshold limit causes direct toxicity to the aquatic flora and fauna.



**Figure 2.2 Effect of heavy metals on living organism (Ahmad *et al.*, 2020)**

The processes of up taking include 1) Biosorption process involves sorption of material in contact via biopolymer or biomaterial. It is found effective in detoxifying heavy metals in lower concentration (Gautam *et al.* 2015). 2) Cellular sites involved in heavy metals bind to the cell surface and are also transported within the cell Fig (2.3), whereas the adsorptions process does not depend on metabolic process, requiring several metal transporters (Barakat 2011). 3) Ion exchange as it is composed of polysaccharides, proteins, and lipids. These constituents contribute to various functional groups (carboxyl, hydroxyl, phosphate, amino, sulfhydryl, amide, alkyl, and aromatic compound) and hence possess an overall negative charge to the cell surface. Monteiro *et al.* (2011) investigated that cell surface of alga acts as a strong binding site for metal cations and is involved in metal exchange through the ion-exchange mechanism during the interaction between metal ion and protein on biological surface, metal ions coordinated in formation of complex groups. However, in marine system, a major part of active sites are bonded with protons at low pH or with alkaline earth metals (Ca, Na, and Mg) at higher pH. In the presence of cations such as  $\text{Cu}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Fe}^{2+}$ , and  $\text{Pb}^{2+}$ , the previously bind protons and metals are released, and these cations are sorbed on cell surface. But in the case of anions, adsorption characteristics of algal significantly change toward the competitive binding of metal ions to the cell surface as shown in Fig (2.4)

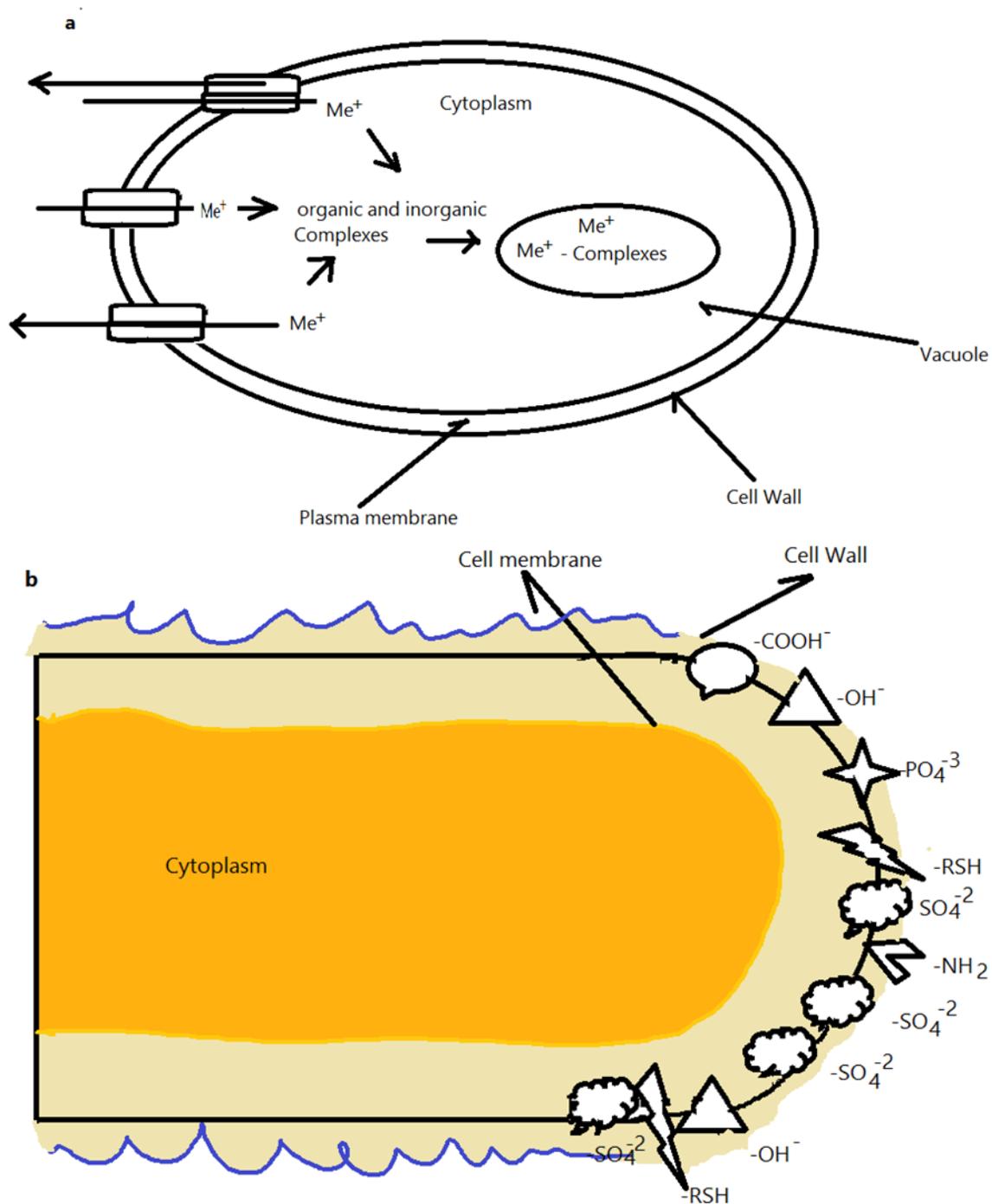


Figure 2.3 Cellular mechanism of HMs: (a) inside the living cell; (b) on the cell surface (Ahmad *et al.*, 2020)

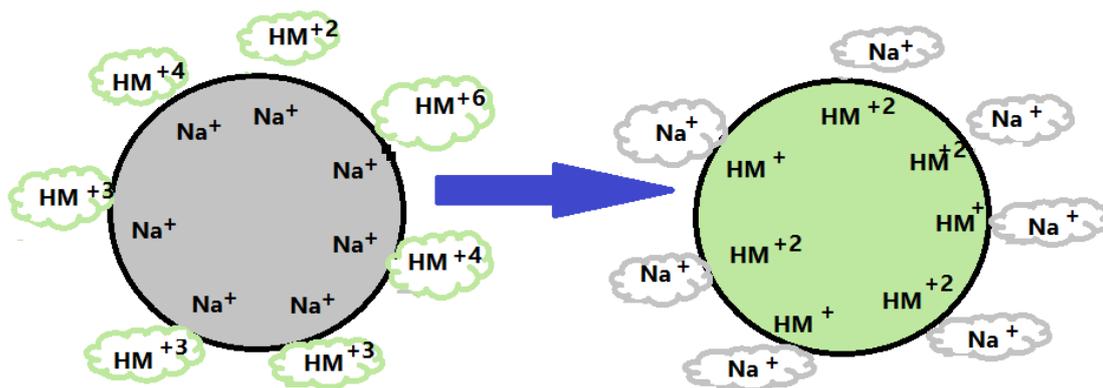


Figure 2.4 Basic principle of ion exchange through living cell (Ahmad *et al.*, 2020)

4) Physical adsorption refers to a phenomenon in which aqueous metal ion binds to polyelectrolytes of algal cell wall through weak force of attraction such as van der Waals force, covalent bonding, redox interaction, biomineralization, etc. (Perpetuo *et al.* 2011). The pH of the adsorbing media has strong influence on the adsorption of the metal ion. It has been found that alkaline pH increases the attraction of metal cations and thus improves their adsorption on cell surface by replacing the functional groups containing negative charge such as polysaccharides, phosphate, amino group of nucleic acid, and amino and carboxyl group of protein (Majumder *et al.* 2015).

## 2.4 Polluted Water Treatment By Algae, Duckweed, and Sorghum

### 2.4.1 Bioremediation of polluted water using duckweed and algae

The bioremediation of surface water polluted by wastewater, with treatment by algae and duckweed are one of the most interesting technologies for removal of the organic and inorganic pollution, they are also economically inexpensive technologies, especially for developing countries (Agamuthu *et al.*,2013). However, the byproduct of both (algae and duckweed) can be used for biofertilizer and biofuel, sometimes the duckweed is the best animal food specifically for poultry.

Bioremediation of polluted water by using algae and duckweed have an advantage by cycling the nutrient to the environment also to improve water quality for irrigation purposes, the basic concept of duckweed polluted water treatment system is to farm local duckweed on the surface water was polluted by wastewater (Zimmo *et al.*,1995). Duckweed has a high mineral absorption capacity and can tolerate high organic loading as well as high concentrations of micronutrients.

Landolt and Kandeler (1987) investigated that the Lemnaceae have the greatest capacity in assimilating the macro-elements N, P, K, Ca, Na and Mg.

Also algae have the same ability as duckweeds to purify the wastewater and they can be used for biofuel and biofertilizer while having faster growth rate compared to other aquatic plants, algae have a role in balancing the (oxygen, carbon and nutrient) cycling by treating wastewater (Barsanti and Gualtieri, 2006).

#### **2.4.1.1 Algae cultivation system for polluted water treatment**

There are three main systems for cultivation of microalgae (open, closed, and immobilized system). The open system is simpler to conduct and cheaper. However, the open system is much affected by environmental factors such as temperature and light intensity. Also, the closed cultivation system is more complex to conduct but the environmental conditions should be controlled for cultivation, and the immobilized system is where algae are trapped in a solid medium (Agarwal *et al.*, 2019; Rathod, 2016).

##### ***Open pond system***

Open pond algal cultivation is more preferable for the cultivation of microalgae for wastewater treatment, some advantage points of such technique includes: the system can be built on a larger scale, it is easy to manage and control, it can be conducted with a low budget and carried out in natural or artificial lake and ponds, as it does not required controlled the environmental factors like light intensity and temperature, (Rathod, 2016). On the other hand, Lantin *et al.* (2012) recorded some disadvantage of the open pond system, the open pond system has the two major designs operated on a large scale and those are (raceway ponds and circular ponds).

##### ***Closed pond photobioreactors***

The close system has a better light penetration than the open system, also it has a high biomass production rate while being less time consuming, but energy is required for a system like that and addition of the CO<sub>2</sub> for algal growth it yes another requirement. Operating close pond system is cost ineffective (Zimmo *et al.*, 1995). The system needs an exchanger for both cooling and heating the system depending on its location. This system has two major classes: tubular reactors and covered raceways (Richmond *et al.*, 1990).

##### ***Immobilized cultivation system***

The immobilized system is where the algae cells are locked in the solid media. However, immobilized systems do not have the harvesting problems, this system can be used for wastewater treatment by trapping the algal cells, commonly the immobilization algae system is

performed in the small scale. Algae cells can remove the nitrate, phosphate and ammonium in the wastewater when treated by immobilization algae system (Chevalier and Noue, 1985). Rathod (2016); Agarwal et al., (2019) reported that *Phormidium laminosum* immobilized on foam polymer has the potential to reduce nitrate in a continuous-flow system with uptake efficiencies above 90%.

#### **2.4.2 Duckweed cultivation system for polluted water treatment**

Duckweed farming process need the open pond system, and requires the nutrient for optimum production and the harvesting frequency carried out during the year in the duckweed farm (Skillicorn *et al.*, 1993).

Cultivation of duckweed in the pond of the polluted water contained a high level of macro and micronutrients and they were quite helpful for duckweed growth and production. Also the cultivation processes should be conducted without using fertilization process (Hasan and Chakrabarti, 2009).

Duckweed has ability to grow on the surface of ponds of 1 to 50 cm deep (Gaigher and Short, 1986), also the large-scale duckweed farm production requires the availability of relatively large quantities of organic waste. In addition, the wastewater treatment by farming the duckweed serves as a good source for inorganic nitrate, phosphate and potassium, where that macronutrients are essential for duckweed growth rate. Moreover, the wastewater was the source of trace elements, Duckweed accumulates 99 percent of nutrients and dissolved the solids in the wastewater (Skillicorn *et al.*, 1993; Spira and Journey, 1993). Hasan and Chakrabarti (2009) established that the byproduct of duckweed biomass was rich in protein for feedstock when tested for availability.

#### **2.4.3 Sorghum cultivation system for polluted water treatment**

Sorghum plant was one of those plants is able to up take the metal and removing the pollutant from the water and soil, especially in the arid regions where using the wastewater for irrigation system in the summer season sorghum use to decreases the pollutant in the soil. Also, sorghu is one of the best “Hyperaccumulators” for the phytoremediation of metal-polluted sites (Karimi, 2013). However, it used for biofuel production, when sorghum irrigated by polluted water was accumulate the high level of toxic metals. Also, the water rich in the N ,P and K encouraging the high biomass of sorghum yield and sugar production, the sugars in the sorghum has an economic advantage over starch-based crops for biofuel use (Goleman *et al.*, 2019). The basic points making the sorghum attractive crop for biofuel technology are: wide range of adaptation salinity tolerant, drought resistant, being a hyper accumulator (Shoemaker and Bransby, 2010).

Sorghum cultivation is carried out in the soil, the plantation can be performed in the wetland pond. Also, for irrigation systems use the polluted water that is rich in nutrients and organic compounds to purify the water, and to produce high biomass of sorghum (Głab and Sowiński, 2019).

## **2.5 Polluted Water**

Polluted water is a type water that is changed in (Physical, chemical, and biological) properties because of human activity, when the human activity needs to consume water in daily life. So, discharging waste such as body waste (feces and urine), food waste (food scarp and fat), household cleaner (detergent chemicals) and dirt, microorganisms (germs), which are hazardous and have damaging effects on the environment via destroying the sustainability, also some phenomenon of water pollution appear in the River water and lake during the discharge of wastewater in the River like (Eutrophication) (Metcalf and Eddy, 1991). Wastewater treatment is the process and technology that is used to remediate most of the contaminants which are affecting the water properties to confirm environmental balancing and good public health. On the other hand, handling the energy from wastewater to reusing it in the biotechnology and renewable energy (Awuah et al., 2009 & Amoatey and Bani, 2016).

### **2.5.1 Polluted water reuse**

Polluted water consists of industrial discharged effluents, sewage water, and the rain water. The use of this type of water is a common practice in agriculture. Polluted water has more application in the world, because of daily discharge of wastewater to the environment, wastewater quantity increases when the population size increases. Furthermore, most of the countries established the new technology and application for reusing polluted water in the different sectors like agricultural and renewable energy, in the same time reducing the CO<sub>2</sub> emission with toxin metal in the ecosystem by sustainable application to protect the environment, also the direct use of polluted water for irrigation have effect on the plant soil and ground water (Sperling, 2015).

#### **2.5.1.1 Polluted water reusing for irrigation**

Land application of waste or polluted water (sludge and excreta) practices are widespread around the world in the many countries, some of them used the sludge for land fertilization or directly use polluted water for irrigation system (Soulie and Tremea, 1991).

Non-treated of surface water polluted with wastewater was used for irrigation in a verity of developing countries based on information from the countries providing data on irrigated area. WHO (2006) investigated that nearly 7 % of the total irrigated land in the world used polluted

water or wastewater for irrigation without treatment, this indicates that nearly 20 million hectare globally irrigated with wastewater (UNHSP, 2008).

Polluted water usage for irrigation system has both advantages and disadvantages. Depending on WHO (2006), reported that polluted water quality should be within the irrigation standard limit for reusable especially for irrigation.

In some developed and developing countries, using surface polluted water for irrigation after pass through the treatment process. Water treatment is the most effective practice in the modern time to prevent health related hazards and environmental pollution through pollute water application. Drechsel et al. (2014), described three stages of polluted water treatment which were; primary, secondary, and tertiary treatments. Also, for instance these three stages depending on the country's ability to treat polluted water, and in the primary and secondary treatment BOD and suspend solid removed in the water. Although the treatment functioning on reusable polluted water from industrial and domestic recycling, to protect the environment from the hazard and toxic organic and nonorganic substances. The process of recycling and removing the toxic nutrient and heavy metals from polluted water by using bioremediation and phytoremediation process( Gnajo *et al.*, 2013), while the byproducts from bioremediation processes include to the biotechnology of biofuel, biofertilizer and biodiesel, in the outlet of bioremediation process the polluted waters are available and suitable for irrigation purposes (Kollmann *et al.*, 2017)

## CHAPTER THREE

### MATERIALS AND METHODS

#### 3.1 Study Area

The study area located in the Tanjaro, Sulaymaniyah Governorate-Iraq, the present study focused on the Tanjaro River. The Tanjaro River starts in the Sulaymaniyah Governorate between the Azmar and Baranan Mountains and runs near the NW to SE border of Sulaymaniyah City towards and feeding Darbandikhan Lake. The river extends from northwest to southeast of Sulaymaniyah City (Fig.1). The sources and the point are feed the Tanjaro River tributaries shows in Table (3.1).

**Table 3.1 Head water locations of the Tanjaro River tributaries**

Tanjaro feeding channel	N (Latitude)	E (Longitude)	Elevation
Chaq-Chaq (Head water 1)	35.596274°	45.380615°	805
Kani-Ban (Head water 2)	35.510044°	45.322975°	705
Sarchnar Stream (Head water3)	35.585677°	45.379832°	762
Bakrajo (Head water 4)	35.52001°	45.36185°	694
Tanjaro ( Head water 5)	35.506220°	45.416535°	643

The Tanjaro River passes through the Tanjaro valley crossing many agricultural regions with a catchment area of 1167.3 km<sup>2</sup>, a length of 66.7 km, and an average slope of 11% (Muhammed, 2002). Darbandikhan Lake water discharges to the Diyala River one of the major tributaries of the Tigris River. the City of Sulaymaniyah supplies the Tanjaro River with 265,000 m<sup>3</sup> of wastewater daily and mixes with sources from the Dokan Dam (112,000 m<sup>3</sup> d<sup>-1</sup>), Sarchnar spring (48,000 m<sup>3</sup> d<sup>-1</sup>) and other sources. The untreated water from Sulaymaniyah sewage is eventually combined with rainwater and discharged through sewer pipelines into the Tanjaro River (Rashid, 2010)

There are several sources of pollution in the Tanjaro River. Much of the sewage comes from the Sulaymaniyah City center. This includes: raw influent (sewage), which comes from household waste liquid such as toilets, baths, showers, kitchens, sinks, etc. disposed via sewers, and municipal wastewater, which originates as residential, commercial, and industrial liquid waste and includes storm water runoff. In addition, the Tanjaro River was polluted from sewage sources (Nature Iraq, 2008) originating from Qalawa, Qiliansan, , Wluba, Bakrajo, Kani Goma, Shekh Abbas, Tanjaro villages, and both legal and illegal factories located on the Tanjaro River.

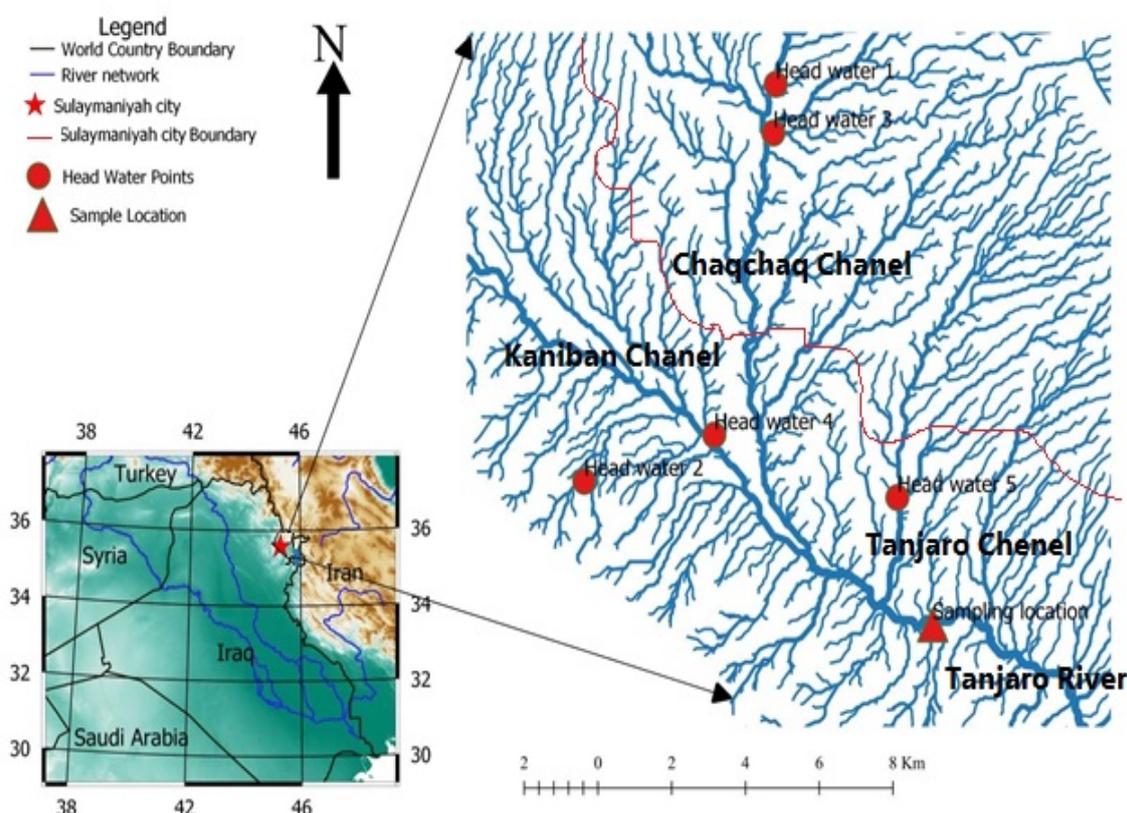
Other potential sources of contamination are runoff from excess irrigation on fields that have applied with pesticides and fertilizers and leachate from the Tanjaro landfill (Fig 3.1b).

Sulaymaniyah sewage outlets include:

- Sewage 1 (Sarchinar): N 35.33099° E 45. 22929°.
- Sewage 2 (Industrial Area): N 35.33223° E 45.2259°. This sewage outlet is located in the industrial area on the southwest side of Sulaymaniyah City. Waste is discharged by the Sulaymaniyah Oil Refining station along with many other factories and houses near the sugar factory quarter in the Qiliasan area of Sulaymaniyah.
- Sewage 3 (Qalawa): N 35.3327° E 45.25326°.
- Sewage 4 (Wluba): N 35.3238.1° E 45.24202°. This discharge comes from houses in Wluba.

Sewage 5 (Shekh Abbas): N 35.3144° E 45.2420.2°.

Tanjaro River water sampling collected from the start point of the Tanjaro River to Darbanikhan Lake, also from wastewater generally used for irrigation by farmer (Fig 3.1a,c). The study area located in the Tanjaro, Sulaymaniyah Governorate-Iraq, and the present study focused on the Tanjaro River water.



**Figure 3.1a** Tanjaro River in Sulaymaniyah city with headwater feeds River and sampling location (prepare by ArcGIS, 10.8)

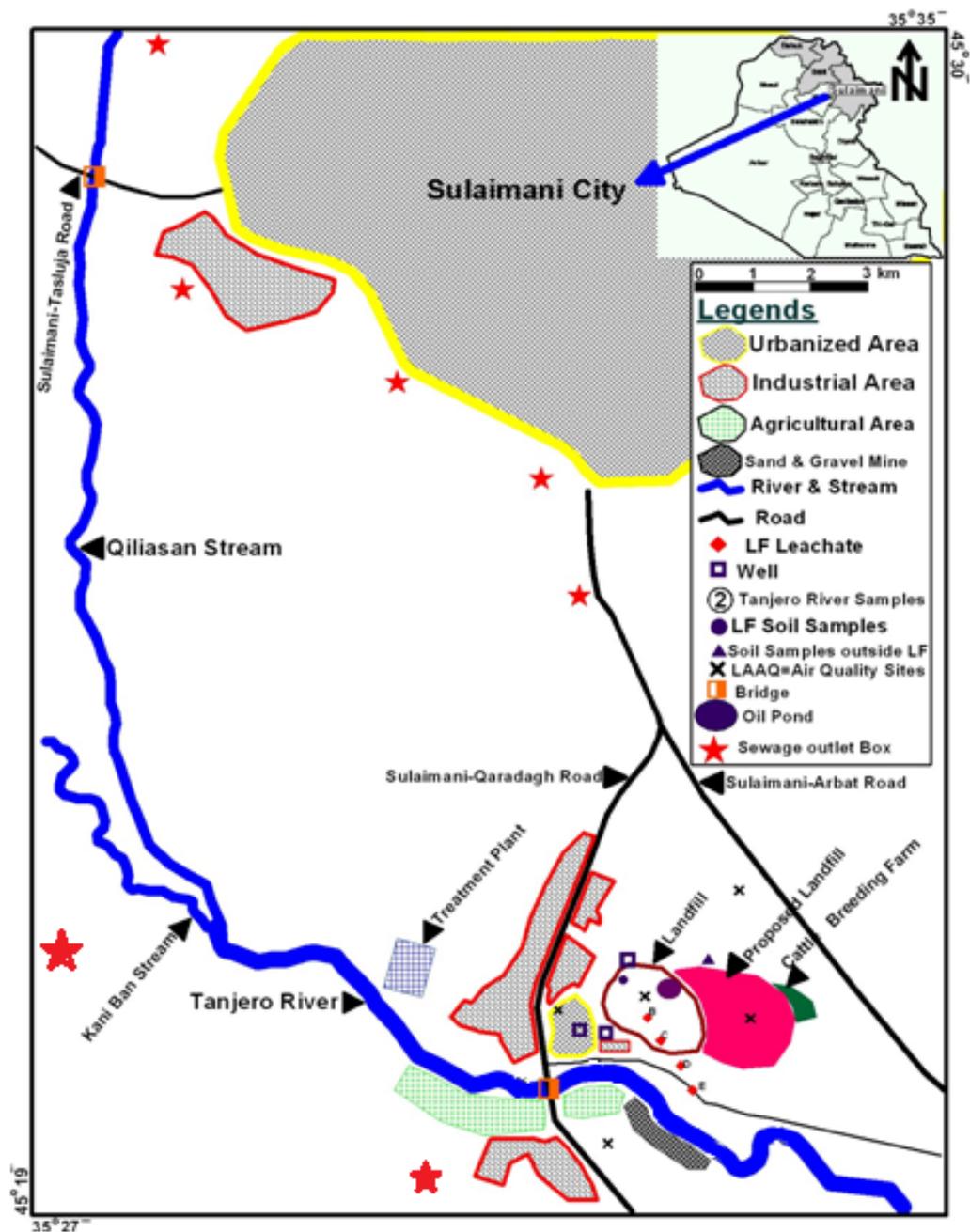


Figure 3.1b Tanjero River surrounding area and Sulaymaniyah city sewage outlet (Rashid, 2010)



**Figure 3.1c** sampling location

## **3.2 Experimental Design**

### **3.2.1 Algae and duckweed experiment**

Six glass basins with specific dimension (aquarium = 50 cm high, 35 cm width 50 cm length) with 87.5 liter of capacity, open system ex-situ technology were used to grow the algae and duckweed in triplicate during the experiment. This basin was filled with 50 liter of water sample from the polluted Tanjaro River. The water sample collected from Tanjaro River one time during algae and duckweed experiment from the farmer pond were used for irrigation in the sampling location as shown in the Fig (3.1a) as a red triangle. The specific conditions controlled for algae and duckweed during experiment such as light and temperature in the greenhouse (Fig 3.2a) . However, sedimentation and filtration harvesting method were conducted after 15 days (Sukenik and Shelef, 1984) (Fig 3.4).

The algae and duckweed were harvested 3 times (0, 5, 10 and 15 day) over the course from (August 1, 2018 to August 15, 2018) of the experiment with 3 times of water sampling to measurement and evaluate the effect of harvesting frequency on remediation of polluted water (Warthington, 2016). During harvesting, both the biomass and the water sampled analyzed.

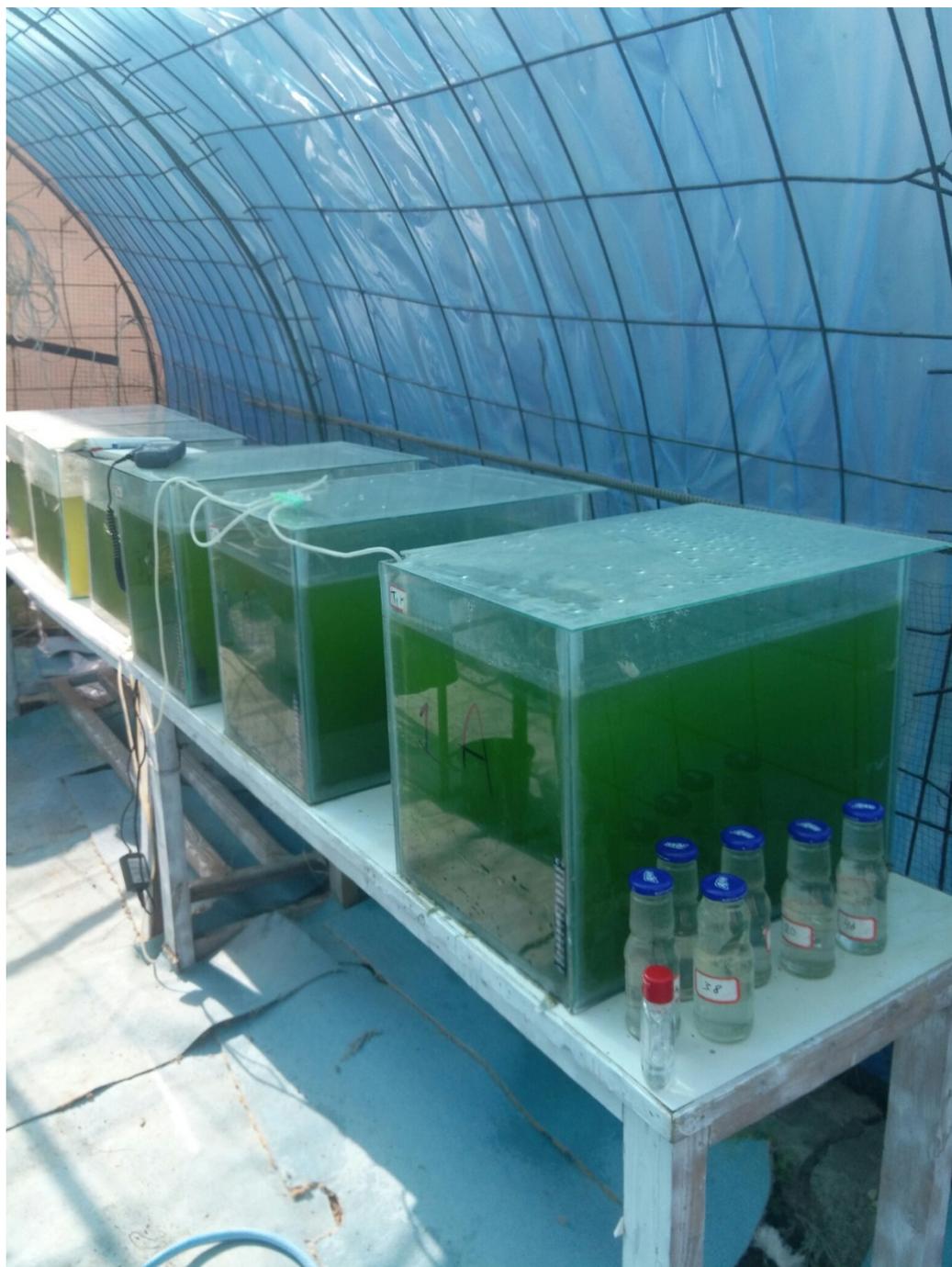


Figure 3.2a Algae and duckweed experiment

### 3.2.2 Sorghum experiment

Special sorghum soil pots was grown separately in large pots with dimension (35cm high, 25cm diameter) with pot capacity 17.5 liter, and 3 replicate of pots (A=1-time irrigation/ week, B= 2-time irrigation/ week, C= 3-time irrigation/ week and Control= no plant) were filled to 15 Kg

of soil from Bakrajo farm and the condition semi controlled in the green house as shown in Fig.(3.3 and 3.4). The soil was air-dried, the coarse fraction (>4 mm of diameter) was removed by sieving, and the fine-earth fraction (<4 mm diameter) was mixed prior to filling the pots to homogenize the samples. The pots were filled as shown in Fig (3.5). Fifteen sorghum (C4 plant, *Sorghum bicolor*) seed planted inside each soil pots, after 3 day of germination the growth sorghum plant thinned to 9 plant inside each soil pots. However, during irrigation frequency (1, 2 and 3-time irrigation/week), for two-month August 1, 2018 to October 1, 2018. The water sampled from Tanjaro River for irrigation during the sorghum experiment 16 times to cover the flood-surface irrigation frequency as shown in Fig (3.4 and 3.5). The drained water from soil pots were collected during the experiment in each irrigation time, and the soil was sampled from the soil pots before the time of each irrigation during the experiment. Both soil and the drained water from soil pots were analyzed as described below in the laboratory measurements. At the end of the experiment, the biomass of sorghum plant harvested and analyzed.

### 3.3 Water Laboratory Analysis

Water laboratory measured consists of physiochemical measurements such as: pH, TDS, DO, BOD, temperature, turbidity,  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{Cl}^-$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ , Fe, Co, Cd, Pb, Cr, Cu, As, Zn and Mn). In addition, the same measurement conducted during the sorghum experiment for irrigation water and drained wtere from soil pot.

#### 3.3.1 Potential of Hydrogen ion (pH) and temperature( $T^\circ\text{C}$ )

To measure the water pH and Temperature  $^\circ\text{C}$ , a portable pH meter HANNA HI 8314 was calibrated and used as described by APHA (1998), at College of Agricultural Engineering Science in the Department of Natural Resources.

#### 3.3.2 Electrical Conductivity (EC) and Total Dissolved Salt (TDS)

Electrical conductivity (EC in  $\text{dSm}^{-1}$ ) and total dissolved salt (TDS  $\text{mgL}^{-1}$ ) of the water sample were measured in the  $25^\circ\text{C}$  by Ec meter WTW, Multi197i at the time of sampling, according to APHA (1998) at the College of Agricultural Engineering Science in the Department of Natural Resources.



Figure 3.3 Sorghum, algae, and duckweed experiment

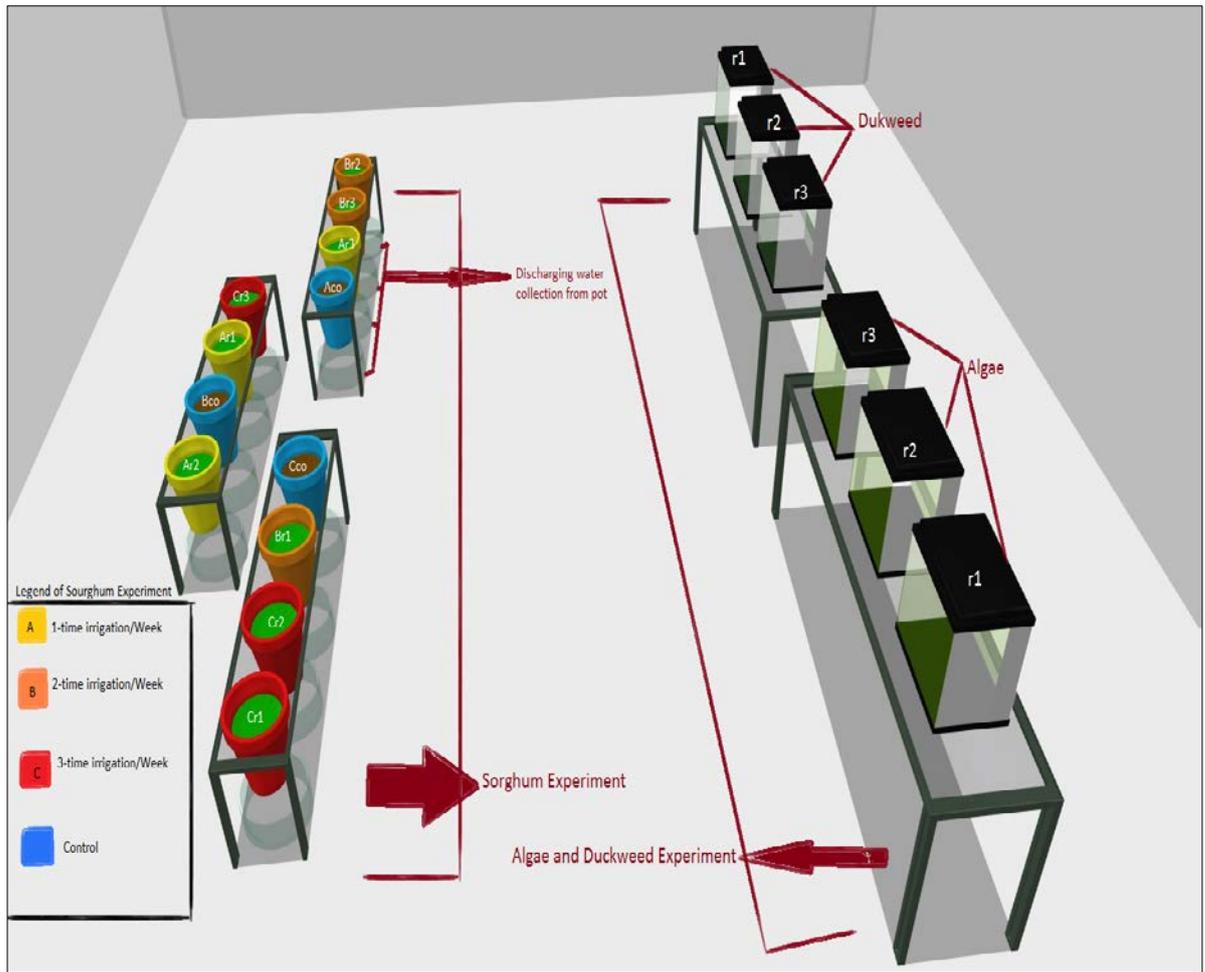
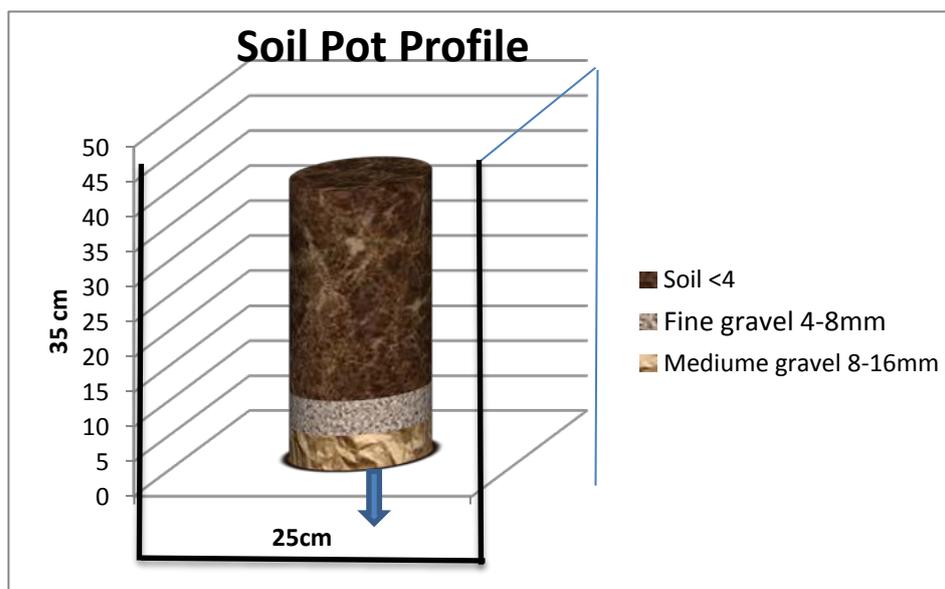


Figure 3.4 Algae, duckweed, and sorghum experiment design



**Figure 3.5 Soil pot schematic for sorghum plant experiment**

### 3.3.3 Turbidity

Turbidity was measured by turbidity meter WTW, pFoto Flex/ photo Flex Turb 430, after calibration with turbidity standards, the results were expressed in terms of nephelometric turbidity unit ((NTU), according to APHA (1998) at College of Agricultural Engineering Science in the Department of Natural Resources .

### 3.3.4 Dissolved oxygen (DO)

Water dissolved oxygen measured at the site using a special oxygen- sensitive membrane electrode WTW, Multi197i, results were expressed in ( $\text{mgO}_2 \text{ L}^{-1}$ ), as described by APHA (1998) at College of Agricultural Engineering Science in the Department of Natural Resources.

### 3.3.5 Biological Oxygen Demand ( $\text{BOD}_5$ )

The biological oxygen demand was determined depending on the dissolved oxygen decreased for 5 day of incubation at  $27^\circ\text{C}$ , by OxiTop control 6, German Standard Method (2000) at College of Agricultural Engineering Science in the Department of Natural Resources.

### 3.3.6 Carbonate ( $\text{CO}_3^{2-}$ ) and bicarbonate ( $\text{HCO}_3^-$ )

Carbonate and bicarbonate in the water sample were determined by acid-base titrimetric method according to APHA, (1998), and results expressed in  $\text{mg L}^{-1}$ .

### 3.3.7 K<sup>+</sup> and Na<sup>+</sup>

Potassium and sodium was measured by PFP7 flam photometer JENAWAY as recommended by APHA (1998), at College of Agricultural Engineering Science in the Department of Natural Resources, and results were expressed in mg L<sup>-1</sup>.

### 3.3.8 Cations (Ca<sup>2+</sup> and Mg<sup>2+</sup>) and metals (Fe, Co, Cd, Pb, Cr, Cu, Zn and Mn)

The collected water sample for determination of Calcium (Ca<sup>2+</sup>) and Magnesium (Mg<sup>2+</sup>), with heavy metals (Fe, Co, Cd, Pb, Cr, Cu, Zn and Mn) were prepared for ICP running . The concentration of cations and metals were detected by Inductively Coupled Plasma mass spectrometer (ICP) Perkin- Elmer/Optical Emission Spectrometer Optima 2100 DV, at the Kurdistan Institution for Strategic Studies and Scientific Research according to APHA (1998). Results expressed in mg L<sup>-1</sup>.

### 3.3.9 Anions (NO<sub>3</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup>)

Anions (NO<sub>3</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup>) of each collected water sample was determined at the Kurdistan Institution for Strategic Studies and Scientific Research using an Ion chromatography (IXS1500 DIONEX)) as recommended by APHA (1998), results expressed in mg L<sup>-1</sup>.

### 3.3.10 Irrigation Water Quality Index

Irrigation Water Quality Index (IWQI) calculated before and after the experiment following Eq. (1, 2) (Asadi *et al.*, 2020). And the percentage of IWQI improvement calculated depending on equation (3), the weighting of each parameter calculating been done by assigning weights (*w<sub>i</sub>*) according to relative importance of each chemical parameter for irrigation water quality according to Ayers and Westcot (1985).

$$W_i = \frac{w}{N} \sum_{i=1}^N R_i \dots\dots\dots(1)$$

$$IWQIndex = \sum W_i \dots\dots\dots(2)$$

$$\% \text{ IWQI improvement} = \frac{fIWQI - iIWQI}{iIWQI} \times 100 \dots\dots\dots (3)$$

Where W is the involvement of each one of the water measurements, w is the weight of the water measurements, N is the total number parameters, and R is the rating value. And iIWQI= initial Irrigation Water Quality Index fIWQI= final Irrigation Water Quality Index. The water suitability for irrigation estimated depending on the three class of the IWQIndex for irrigation, when lower than 19 was specified as low suitability for irrigation, between 19 and 32 as medium, and higher than 32 as high suitability for irrigation (Asadi *et al.*, 2020)..

### 3.3.11 Metal Removal Efficiency (MRE)

Metal Removal Efficiency (MRE) calculated depending on equation (4) (Majeed, 2017).

$$\text{MRE} = \frac{iC - fC}{iC} \times 100 \dots\dots\dots(4)$$

Where iC= initial concentration and fC= final concentration

### 3.3.12 Biological accumulation Coefficient (BAC), Biological concentration Factor (BCF), Biological Extraction Factor (BEF) and Translocation Factor (TF)

Biological Accumulation Coefficient (BAC) for sorghum was calculated as the ratio of heavy metal content in sorghum shoots to the total metal content in the soil and the (BAC) for algae and duckweed were calculated as the ratio of heavy metal content in algae and duckweed biomass to the total metal content in the water given in equation 5. Biological Concentration Factor (BCF) was calculated as metal concentration ratio of plant roots to total metal content in soil given in equation 6 (Yoon *et al.*, 2006). Biological Extraction Factor (BEF) was calculated as metal concentration ratio of plant roots to total metal content in soil given in equation 7, Translocation Factor (TF) was described as ratio of heavy metals in plant shoot to that in plant root given in equation 8 (Cui *et al.*, 2007)

$$\text{BAC} = \frac{\text{Shoots} + \text{Roots (biomass) Metals}}{\text{Soil or Water Metals}} \dots\dots\dots(5)$$

$$\text{BCF} = \frac{\text{Roots Metals}}{\text{Soil Metals}} \dots\dots\dots(6)$$

$$\text{BEF} = \frac{\text{Shoots Metals}}{\text{Soil Metals}} \dots\dots\dots(7)$$

$$\text{TF} = \frac{\text{Shoots Metals}}{\text{Roots Metals}} \dots\dots\dots(8)$$

### 3.3.13 Algae enumeration and examination in the water

The algae enumeration was carried out, when the water samples were collected for algae and duckweed experiment. The method of Most Probable Number (MPN) was used to count the viable cell of algae in the water. However, the MPN method was used one time during the experiment according to (Bellinger and David, 2015). In addition, the algae growth rates in the harvesting frequency measured according to chlorophyll *a* during the experiment by using Lamda 25 UV/VIS Spectrophotometer PerkenElmer, as described by Dere *et al.* (1998). The algae examined by preparing the slid under Digital Microscope LABOMED Digiplus, the

microscopic image of algae was identified by Farkha (2018)<sup>1</sup>, the species were introduced under green algae and cyanobacteria were most abundance species (Appendix 15a to 15i).

### 3.4. Soil Laboratory Measurements

Soil samples were collected before the experiment of sorghum, the soil sample was air-dried and passed through (2mm) sieve to prepare for the analysis of total and water-soluble; cations, anions and heavy metals. The aqua regia method was used for determination of total heavy metal concentrations according to Santos et al. (2013). Also, the parameter determined in the soil sample are: pH, EC, TDS, base cation ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ), major anion concentrations ( $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{PO}_4^{3-}$ ), soil organic carbon, total nitrogen, water content), the soil laboratory measurements were performed at the University of California – Riverside.

#### 3.4.1 Soil total aqua regia digestion

Soil samples was collected during the experiment and the samples were run at the University of California – Riverside. The soil samples were ground in an agate mortar and pestle until the sample passes through a (or 0.15 mm) sieve, also weigh 0.25 g of the ground soil sample, and the aqua regia solution 1:3 HCL:HNO<sub>3</sub> were add to the sample, the microwave Anton Paar Multiwave PRO instrument, were used according to digestion procedure was described in the EPA 3052 (1996).

The total cation and heavy metal ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ , P, Fe, Co, Cd, Pb, Cr, Cu, As, Zn and Mn) were determined in the soil sample by Inductively Coupled Plasma mass spectrometer (ICP) Perkin Elmer Optima 7000 DV ICP-OES) at the University of California – Riverside.

#### 3.4.2 Water soluble cation and heavy metals in the soil

A two gram of (<2mm) soil sample was used to determine the water soluble cation and heavy metals during the sorghum pot experiment, the 1:1 soil: water ratio was performed, however the same cation and heavy metals ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ , P, Fe, Co, Cd, Pb, Cr, Cu, As, Zn and Mn) were detected by Inductively Coupled Plasma mass spectrometer (ICP) Perkin Elmer Optima 7000 DV ICP-OES, at the University of California – Riverside, as described by Margesin and Schinner (2013).

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<sup>1</sup> During an interview conducted on October, 2018, Assist Prof. Dr. Farkha K.T. she examines the microscopic image of algae (Prescott, 1978 ;1982)

### 3.4.3 Potential of hydrogen ion (pH) and Electrical conductivity (EC) in the soil

The pH and Ec in the soil sample were measured in the (1:1) soil: water ratio, The pH and EC 1:1 (W/V) were measured at the University of California – Riverside according to the procedure was described in the Soil Survey Staff (2014).

### 3.4.4 Soil organic Carbon and Nitrogen

Total organic carbon and total nitrogen were determined by CN analyzer Thermo CE Elantech Flash EA 1112, at the University of California – Riverside according to the procedure was described in the Flash EA 1112 (2007).

## 3.5 Algae, Duckweed and Sorghum Laboratory Measurements

### 3.5.1 Biomass measuring

#### 3.5.1.1 Sorghum biomass measuring

The plant sorghum biomass was harvested in the end of the experiment. The sorghum biomass per pot calculated depending on the total dry weight (*TDW*), according to equation (9) as described by Bell and Fischer (1994)

$$TDW = \frac{SDW}{SFW} \times TFW \dots\dots\dots(9)$$

Where *TFW*=Total Fresh Weight, *SFW*= plant Sample Fresh Weight, and *SDW* =plant Sample Dry Weight.

#### 3.5.1.2 Algae and duckweed biomass measuring

The Algae biomass was harvested three times during experiment, depending on the harvesting frequency by sedimentation and filtration method as recommended by Rathod (2016) to monitoring the aquarium biomass growth rate and measuring the optical density (OD) of algae cell depending on the chlorophyll *a*. The chlorophyll *a* was determined by using Lamda 25 UV/VIS spectrophotometer PerkenElmer, depending on equation (10), and the method recommended by Dere et al. (1998).

$$\text{Chlorophyll } a = 11.75 A^{662} - 2.350 A^{645} \dots\dots\dots (10)$$

Duckweed biomass was measured depending on the growth of duckweed in the aquarium surface area, at the three harvesting time the biomass of duckweed was collected and drying by oven at 48 to 65°C for 48 hr as described by Landolt and Kandeler (1987) the biomass calculated depending on equation (9).

### 3.5.2 Plant Total cation and heavy metals determination

To check the availability of plant for remediation. The (sorghum, duckweed and algae) biomass were drying and grounded by plant tissue grinder until the sample pass through a (0.85 mm) sieve, also weigh 0.25 g of ground tissue sample, and the aqua regia solution 1:3 HCL:HNO<sub>3</sub> were added to the sample, the microwave Anton Paar Multiwave PRO were used according to digestion procedure was described in the EPA 3052. The total cation and heavy metal (Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup>, P, Fe, Co, Cd, Pb, Cr, Cu, Zn and Mn) were determined in the plant tissue sample by Inductively Coupled Plasma mass spectrometer (ICP) Perkin Elmer Optima 7000 DV ICP-OES, at the University of California – Riverside.

### 3.5.3 Plant organic carbon and total nitrogen

Total organic carbon and total nitrogen determined by CN analyzer Thermo CE Elantech Flash EA 1112, at the University of California–Riverside according to procedure was described in the Flash EA 1112 (2007).

### 3.6 Statistical analysis

The study was setup as a completely randomized design repeated (CRD) measures experiment with three replicate, statistical analyses were conducted using the R 3.2.3 software (R core team, 2018) run under "spearman" test at level (0.05), to compare the efficiency of (microphytes: green algae (*Chlorophyta*) and blue-green algae (*Cynobactria*); macrophytes: duckweed (*lemmna Gibba*) and sorghum (*Sorghum Bicolor*) on the remediation of polluted water and shown the efficiency of harvesting and irrigation frequency for both experiment.

## **CHAPTER FOUR**

### **RESULTS AND DISCUSSIONS**

#### **4.1 Algae and Duckweed Bioremediation Experiments**

This experiment conducted to evaluate the capacity of aquatic macro/microphytes to remediate the Tanjaro River water.

##### **4.1.1 Physiochemical measurements in the Tanjaro River**

###### **4.1.1.1 Temperature**

The temperature mean value of water samples were collected from Tanjaro River ranged between 22.67 °C to 27.87 °C during the algae and duckweed experiment as shown in the Table (4.1). The temperature mean value of untreated water was 22.67 °C before the cultivation of algae and duckweed. This temperatures value is optimal for (algae and duckweed) growth rate in the aquarium according to Liu et al. (2018); Barsanti and Gualtieri (2006). Through the experiment, the mean value of water temperature increased in both aquarium of algae and duckweed and the maximum temperature recorded was 27.87°C in the third time of algae biomass harvesting (15 days of cultivation). The increasing of water temperature may signify to the air temperature, also effect of day time sunlight scattering inside of the aquarium, additionally, there are many factors effect on the temperature such as; photosynthesis process by algae and duckweed, biological activity of the microorganisms in the water inside the aquarium, a chemical reaction between the metal and metalloid (Vona *et al.*, 2004 ).

###### **4.1.1.2 Potential of the hydrogen ion (pH)**

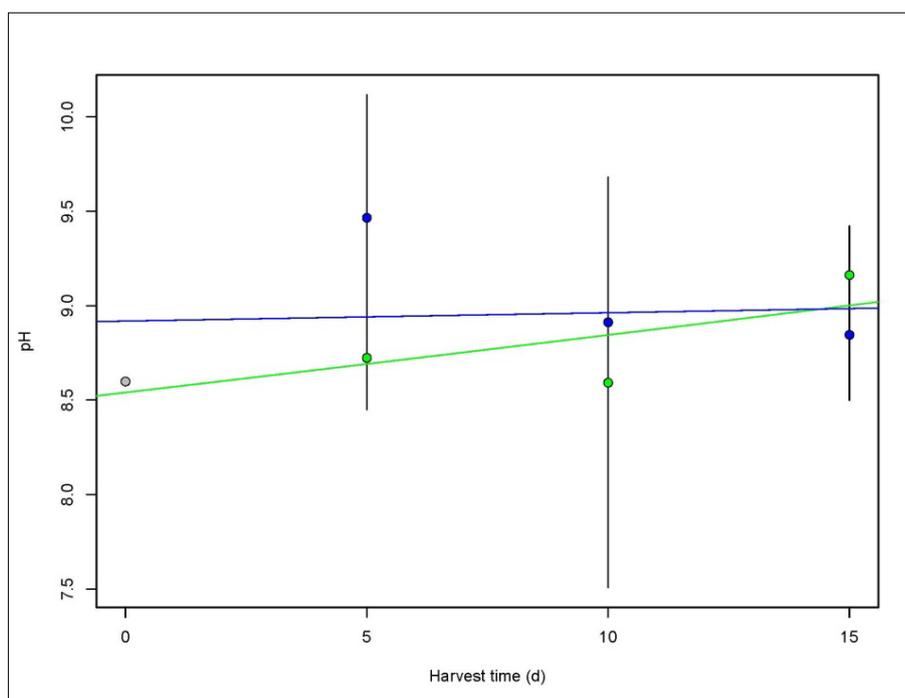
The pH mean value was 8.60 for water before cultivation for both (algae and duckweed). Depending on the Rathod (2016); Caicedo et al. (2000), this value of pH was a peak value for algae and duckweed growth. The mean value of pH in the algae aquarium decreased in the first and second time of algae biomass harvesting as showed in the Table (4.1), but in the third time of the algae biomass harvesting the pH value in the during treated water increased and the value was more than the untreated water. However, in the duckweed aquarium, the pH value increased and recorded the maximum value in the first time of duckweed biomass harvesting, also the value of pH decreased in the second and third time in comparison to the first time of duckweed

biomass harvesting. This changing of pH is predictable, according to Porath and Pollock (1982); Azov (1982) value increases during microalgae and duckweed cultivation due to photosynthetic of CO<sub>2</sub> assimilation. In addition, through absorption of nitrogen by microalgae and duckweed, due to nitrate reduction to ammonia produces one OH<sup>-</sup> ion. Although the increase of pH value causes the precipitation of phosphate (Rathod, 2016).

**Table 4.1 Means value of physiochemical measurements in the untreated water sample from polluted Tanjaro River and during cultivation of algae and duckweed experiment**

Treatment	Harvesting frequency (Cultivation period/day)	T °c	pH	EC dS m <sup>-1</sup>	TDS mgL <sup>-1</sup>	Turbidity NTU	DO mgL <sup>-1</sup>	BOD <sub>5</sub> mgL <sup>-1</sup>	Chlorophyll <i>a</i> mgL <sup>-1</sup>
Untreated water	Before cultivation (Zero day)	22.67	8.60	1.06	558.00	99.07	0.09	10.63	8.43
Algae	harvest 1 (5 day)	24.53	8.58	0.83	159.00	13.90	8.66	7.93	61.07
	harvest 2 (10 day)	24.13	8.59	0.60	163.33	4.75	2.43	7.03	62.81
	harvest 3 (15 day)	27.87	9.16	0.59	131.00	1.86	2.28	22.90	15.43
Duckweed	harvest 1 (5 day)	23.80	9.47	0.72	191.33	29.73	9.64	7.23	79.30
	harvest 2 (10 day)	24.77	8.91	0.65	169.67	2.95	2.57	9.23	7.23
	harvest 3 (15 day)	23.50	8.85	0.65	172.67	1.60	1.46	25.07	2.74
Recommend Max concentration (FAO, 1985)		-	6.5-8.4	0-3	0-2000	-	-	-	-

The present research study supported the increasing of pH value as shown in the Table (4.2) decreasing of (NO<sub>3</sub><sup>-</sup> and PO<sub>4</sub><sup>3-</sup>) concentration during the algae and duckweed experiment. The relationship between pH value in wastewater sample from Tanjaro River and harvesting time (0, 5, 10, 15 days) are shown in Fig (4.1). Depending on the non-linear regression of error bar the results showed a positive relation between pH and harvesting time. Once the cultivation time increased the pH value increased, also the weak relationship refers to photosynthesis and respiration of algae and duckweed for the period of day and night time, this process affected on the CO<sub>2</sub> equilibrium in the water (Cole and Prairie, 2009). There is non-significant difference between algae and duckweed intended of pH increasing during the harvesting time, the positive effect of algae was more than the duckweed depending on the r<sup>2</sup> (Appendix 1). The results agree with Zimmo (2005) were they found pH stability during wastewater treatment by algae and duckweed.



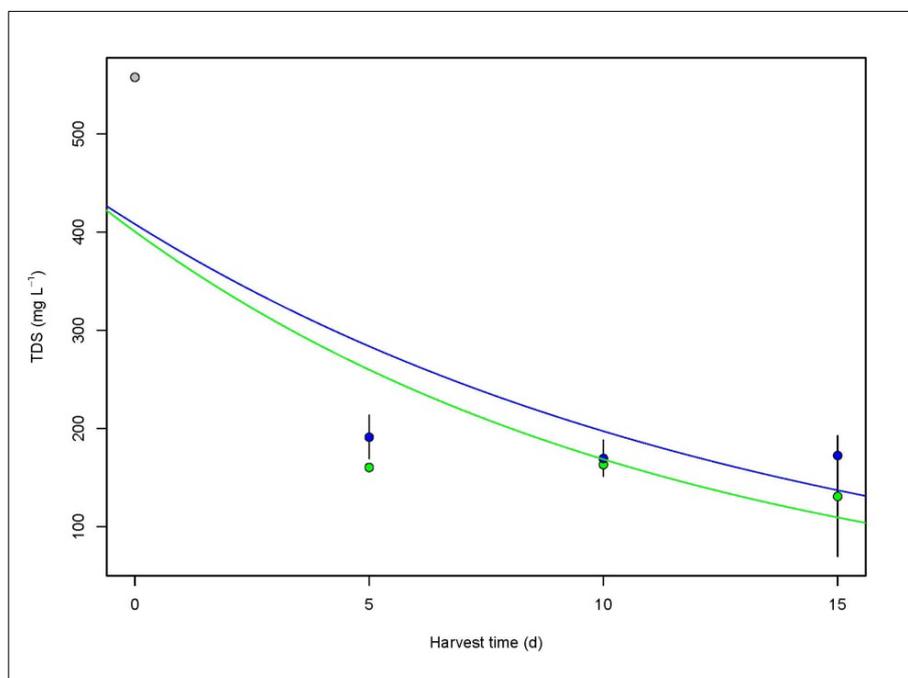
**Figure 4.1** Relationship between pH value in the water sample from Tanjaro River and harvesting time (0, 5, 10, 15) per day, by using non-linear regression function in R, the color illustrated untreated water= gray, algae= green, and duckweed= blu

#### 4.1.1.3 Electrical Conductivity ( $EC_{25^{\circ}C}$ ) and Total Dissolved Salts (TDS)

The mean value of EC between 1.06 to 1.06  $dS\ m^{-1}$  in the untreated water sample from Tanjaro River before cultivation of algae and duckweed (Table 4.1). After cultivation of both algae and duckweed the mean value of Ec decreased, and the lowest values (0.59 and 0.65  $dS\ m^{-1}$ ) respectively, for algae and duckweed in the third time of biomass harvesting.

The untreated water means value of TDS is 558.0  $mgL^{-1}$  in the water sample from Tanjaro River, and the value decreased during the algae and duckweed experiment (15 days of cultivation). In addition, the lowest value is 131.00  $mgL^{-1}$  in the third-time of algae biomass harvesting (15 day of cultivation), besides the duckweed was recorded the lowest value (169.67  $mgL^{-1}$ ) of TDS in the second-time of biomass harvesting (10 days of cultivation). The decrease of Ec and TDS after bioremediation experiment is a good indication for total dissolved salt removing from Tanjaro River water. According to Fakhry et al. (2015) & Raiz et al. (2018), they investigated that all species of microalgae have the responsibility for salinity; they can grow under the condition of salinity and increase of the lipid producing in the algae cell by increasing the salinity of the water. The result shows that the algae have the capability for total dissolved salt removing in the water from Tanjaro River to meet the standard limit for irrigation.

However, the duckweed has a positive effect to decreases the salinity in the polluted water. According to Khondker et al. (1993) the Ec is the most important parameter for duckweed grows, duckweed produced high biomass in the high salinity, due to this way the duckweed can remove and uptake the dissolved salt in the water sample from Tanjaro Rive.

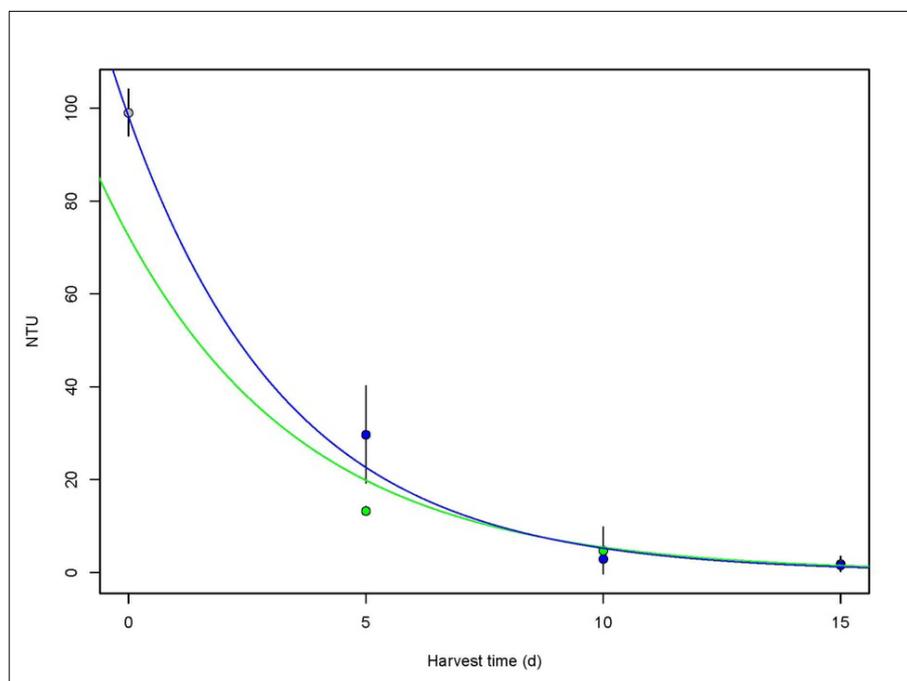


**Figure 4.2 Relationship between TDS mgL<sup>-1</sup> in the water sample from Tanjaro River and the harvesting time (0, 5, 10, 15) per day, by using non-linear regression function in R, the color illustrated untreated water= gray, algae= green, and duckweed= blue**

Furthermore, the results of bioremediation (Algae and Duckweed) showed that there are negative relations between EC and TDS in the water sample from Tanjaro River with harvesting time of algae and duckweed (during cultivation). While by increasing the time of cultivation the dissolved salt decreased in the wastewater from Tanjaro River were used for the experiment, also there is a non-significant difference between algae and duckweed to decreasing the dissolved salt, except day 5 (Fig.4.2). The results showed that the capability of algae and duckweed to remove dissolved salt in the Tanjaro River with significant differences between untreated water with time of harvesting of algae and duckweed (Khondker *et al.*,1993 and Raiz *et al.*,2018).

#### 4.1.1.4 Turbidity

The mean value of turbidity decreased during algae and duckweed experiment as showed in the table (4.1). The lowest mean values (1.60 and 1.86 NTU) were recorded in the third time of duckweed and algae biomass harvesting respectively. In addition, result in this study indicated that there is negative relation between turbidity and harvesting time (Fig.4.3), where algae and duckweed cultivation time increased, the turbidity decreased in the wastewater from Tanjaro River. While, there are non-significant differences between algae and duckweed for turbidity reduction during the time of cultivation (15 days), except the 5 days of cultivation showed significant differences, and there are significant differences between untreated water with harvesting time for both algae and duckweed. Depending on Riaz et al. (2018), they studied the algae capability to improve the polluted water physiochemical quality, and concluded the turbidity decreasing with total dissolved salt during 30 days of the experiment; however, they investigated the positive relation between the turbidity and salinity with TDS where wastewater treated by algae. In addition, Ozengin and Elmaci (2007) they used duckweed to treat 50 L of wastewater in the laboratory experiment for 30 days and they found the ability of duckweed to reduce the turbidity 93%, also investigated that duckweed ability to decrease the turbidity due to reducing the total dissolved salt through adsorption of colloidal materials. Our present results have showed agreement with Ozengin and Elmaci(2007)& Riaz et al.(2018).



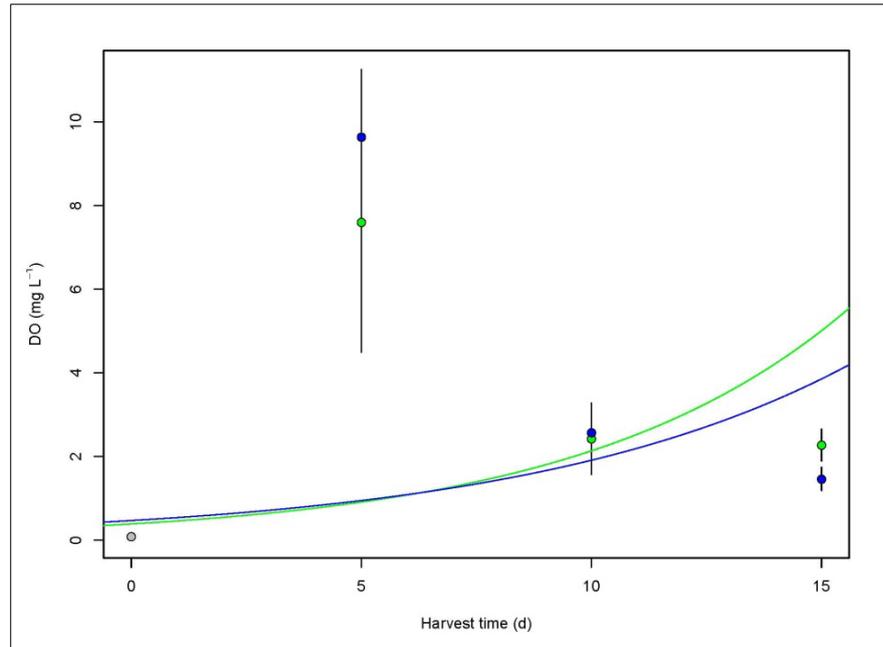
**Figure 4.3 Relationship between Turbidity NTU in the water sample from Tanjaro River with harvesting time (0, 5, 10, 15) per day, by using non-linear regression function in R, the color untreated water= gray, algae= green, and duckweed= blue**

#### 4.1.1.5 Dissolved oxygen (DO) and Biological Oxygen Demand (BOD<sub>5</sub>)

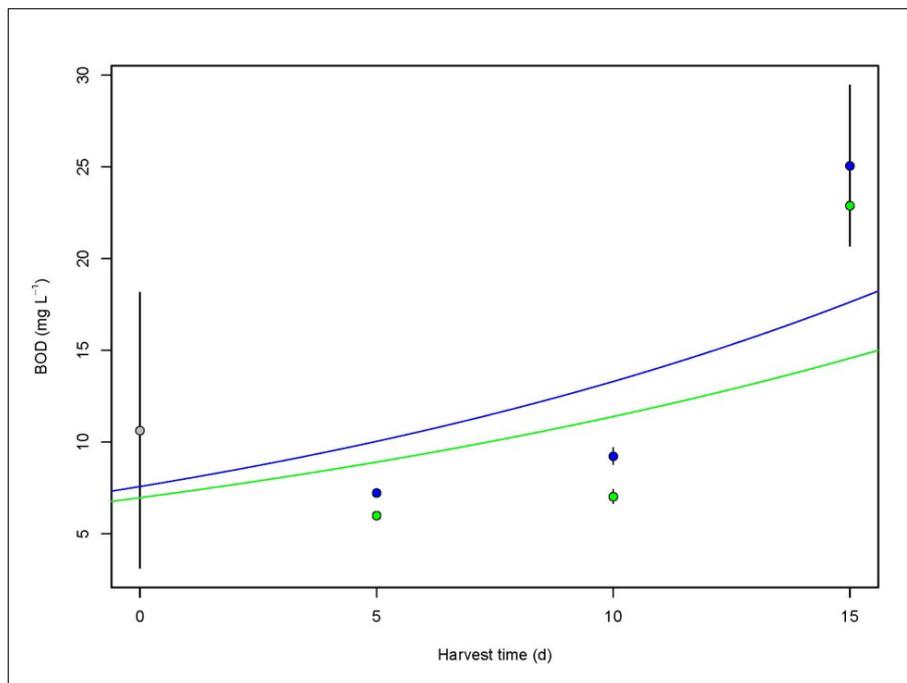
The mean value of dissolved oxygen in the water sample from Tanjaro River before treatment was  $0.09 \text{ mgL}^{-1}$ , this value was increased after bioremediation of water sample by algae and duckweed. The maximum mean value of DO were recorded in the first time of algae and duckweed biomass harvesting and the value are ( $8.66$  and  $9.64 \text{ mg L}^{-1}$ ) respectively, as shown in the Table (4.1). The value of DO was decreased in the second and third time of algae, duckweed biomass harvesting, on the other hand, the value of BOD in the untreated water is ( $10.63 \text{ mg L}^{-1}$ ), and decreased in the algae aquarium during the experiment, except the third time of algae biomass harvesting, the BOD of the water was increased. When the DO is high, the value of BOD decreased and vice versa. The increasing of BOD in the third harvesting of the algae and duckweed biomass referred to the increasing of organic matter in the aquarium, in the third harvesting the biomass of both algae and duckweed start to decompose depending on the decreasing of the nutrient in the aquarium and the microbial activity was increased (Waziri *et al.*, 2010). According to Bhat and Hiremath (2003) were investigated the positive relation between the BOD and organic matter in the wastewater.

The Fig (4.4 a: b) showed the positive relationship between DO and harvesting time of algae and duckweed, by increasing of cultivation time the DO increase in the aquarium. In addition, there are the non-significant difference between algae and duckweed in DO increasing, also in the 5 days of harvesting (Fig.4.4a) shows significant differences for both duckweed and algae between with other harvesting time. Increasing of DO in the algae and duckweed aquarium refers to the chlorophyll *a* appendix (2). On the other hand, there is a positive relationship between BOD and harvesting time (Fig4.4b), when the cultivation increased the BOD value increases; also, significant difference between algae and duckweed in the BOD value depending on the harvesting time, except 3 (15 day of cultivation) time of harvesting. The results in Fig(4.4 b) showed significant difference between algae and duckweed in the 5 and 10 day of experiment.

The correlation between the DO and water BOD is negative as shown in the appendix (3c), also depending on the correlation test the  $r^2$  is (-0.44) (appendix 3 a; b). The present results were showed agreement with Waziri *et al.* (2010) where they studied the interrelation between dissolved oxygen and biological oxygen demand in the wastewater, and they investigated the negative relation between BOD and DO.



**Figure 4.4a** Relationship between DO in the water sample from Tanjaro River with harvesting time (0, 5, 10, 15) per day, by using non-linear regression function in R, the color untreated water= gray, algae= green, and duckweed= blue



**Figure 4.4 b** Relationship between BOD in the water sample from Tanjaro River with harvesting time (0, 5, 10, 15) per day, by using non-linear regression function in R, the color untreated water= gray, algae= green, and duckweed= blue

#### 4.1.1.6 Chlorophyll a

The chlorophyll *a* is an indication for algae and duckweed growth rate in the aquariums as shown in the Table (4.1) the mean value of chlorophyll *a* in the untreated water from Tanjaro River before algae and duckweed cultivation is (8.43 mg L<sup>-1</sup>). In the algae aquarium concentration of chlorophyll *a* increased in the first and second harvesting of the algae biomass harvesting, except the third-time of harvesting was decreased (Appendix 2). Also decreasing of the chlorophyll *a* refers to decreasing of the algae biomass in the aquarium and nutrient availability.

Our results agree with Desortov (1981) was studied the relation between biomass, nutrient availability and chlorophyll *a*, they found a strong relation between algae and phytoplankton biomass with chlorophyll *a*, furthermore, investigated the nutrient availability affecting on chlorophyll *a* was found a positive relation between nutrient especially phosphate and chlorophyll *a*.

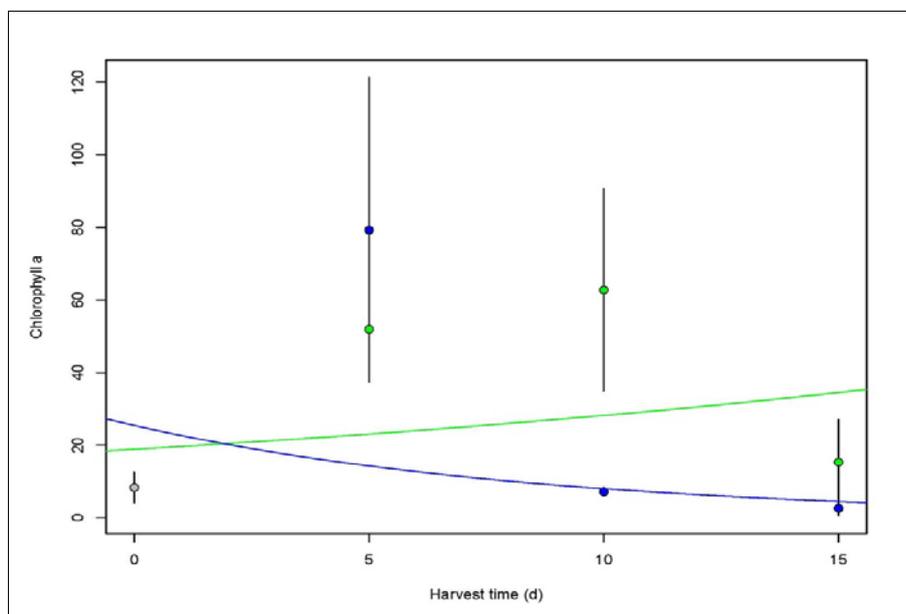
The concentration of chlorophyll *a* in the duckweed aquarium was increased and the maximum concentration in the first time of duckweed biomass harvesting, from the second harvesting the concentration of chlorophyll *a* decreased (Appendix2). The different value of the chlorophyll *a* in the bioremediation experiment was an indication of the photosynthesis activity in the aquarium, and biomass production of the algae and duckweed.

Furthermore, the correlations between chlorophyll *a* and physiochemical measurements were showing in the appendix (3 a; b), Depending on  $r^2$  the order of (strong to weak) negative correlation between chlorophyll *a* and physiochemical measurements are (BOD> Co> NO<sub>3</sub>> TDS> Cu> Fe). Results showed that this parameter decreased in the aquarium when the chlorophyll *a* increased, may be due to up taking, or used by algae and duckweed for metabolic activity. According to Zhou et al. (2016) discussed the Fe as an important micronutrient for algae growth rate and have important role in physiological metabolism and the enzymatic reaction of algae, in addition, Fe concentration use as micronutrient by duckweed (Hasan and Chakrabarti, 2009). Although, Buayam et al. (2019) in there research study found that green microalgae have tolerated capability against Cu in the growth media, they found metabolically Cu is an essential micronutrient for algae growth. Furthermore Gulamiourmi and Soltani (2014) they found the activity of Co concentration for algae pigment (chlorophyll a, b and total chlorophyll), may this cause the algae to take up the Co concentration in the aquarium

On the other hand, the order (strong to weak) positive correlations are (DO> NTU> CO<sub>3</sub>> pH> Cr> SO<sub>4</sub>> PO<sub>4</sub>> Zn> HCO<sub>3</sub>> As). These results are expectable, due to increasing of chlorophyll *a* the DO increased in the media through respiration and photosynthesis increase of turbidity due to increasing of greenish of color in the water. However, HCO<sub>3</sub><sup>-</sup> increasing refers to the pH

value by adding the  $\text{OH}^-$  ion from respiration activity. Desortov (1981), found the positive relationship between nutrient availability and chlorophyll production in the algae and phytoplankton. According to Volland et al. (2014), they found the capability of algae to accumulate the Cr in form of iron-oxygen compound (minerals form), and localization in the cell wall, the results showed that via increasing of chlorophyll *a* increase the algae biomass and this mean that increase the Cr concentration in the aquarium in the form of biomass. In addition, Nadiia et al. (2013) found the Cr (III) in the duckweed cell. Heidarpour et al. (2019) they found the high growth rate of algae when treated by  $100 \text{ mg Zn L}^{-1}$  and Zn one of micronutrient rolling in the plant immune system.

The effect of harvesting time on chlorophyll *a* as shown in the Fig (4.5) there are the positive relationship between algae and harvesting time, when the period of algae cultivation increases the chlorophyll *a* increase. On the other hand, the relation between duckweed and harvesting time is negative relation, when the cultivation time increased the chlorophyll *a* decreased. However, there is the significant difference between algae and duckweed in the chlorophyll *a* concentration in the 10 day of harvesting. The concentration of chlorophyll *a* in the algae treatment was more than the duckweed except for 5 day of harvesting the duckweed has the maximum concentration of chlorophyll *a* (Fig 4.5), it means that algae growth rate and chlorophyll *a* production higher than duckweed. And there is significant difference between zero day with 5 and 10 day of both algae and duckweed cultivation.



**Figure 4.5 Relationship between chlorophyll *a* in the water sample from Tanjaro River with harvesting time (0, 5, 10, 15) per day, by using non-linear regression Coefficient function in R, the color untreated water= gray, algae= green, and duckweed= blue**

#### 4.1.2 Anion ( $\text{HCO}_3^-$ , $\text{CO}_3^{2-}$ , $\text{Cl}^-$ , $\text{NO}_3^-$ , $\text{PO}_4^{3-}$ and $\text{SO}_4^{2-}$ ) concentration in water sample from Tanjaro River during algae and duckweed experiments

##### 4.1.2.1 Bicarbonate ( $\text{HCO}_3^-$ ) and Carbonate ( $\text{CO}_3^{2-}$ )

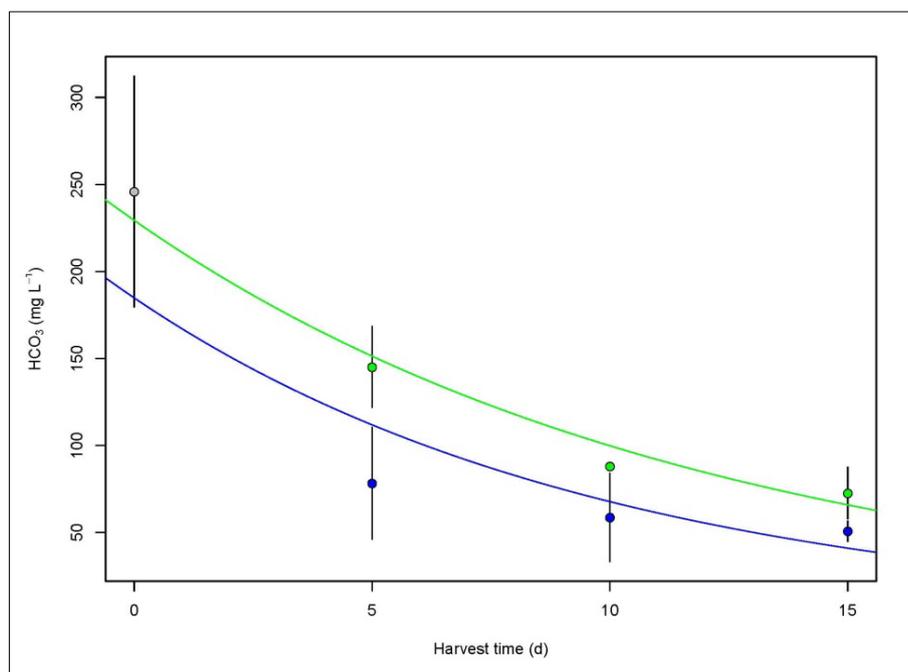
Bicarbonate concentration in the untreated water sample is ( $245.91 \text{ mgL}^{-1}$ ), the concentration of  $\text{HCO}_3^-$  for both algae and duckweed decreased during the processes of the experiment. The lowest mean value of  $\text{HCO}_3^-$  concentration recorded in the third time algae and duckweed biomass harvesting, as expressed in Table (4.2), the concentration is ( $50.76$  and  $72.56 \text{ mgL}^{-1}$ ) in duckweed and algae aquarium respectively. Results of  $\text{HCO}_3^-$  concentration during the algae and duckweed treatment agreed with the results of El-Kheir et al. (2007) & Jahan et al. (2014) were they found the  $\text{HCO}_3^-$  decreasing in the polluted water were treated by algae and duckweed. Also from the appendix (3 a; b) showed a negative relationship between pH and  $\text{HCO}_3^-$  in the water of aquarium, where the pH increased the concentration of  $\text{HCO}_3^-$  decreased (Wurts and Durborow, 1992), except the third-time of algae harvesting. In the estimation for the relation between  $\text{HCO}_3^-$  and harvesting time, results showed a negative relation (Fig 4.6 a), explained that; when the time of cultivation increases the reduction of  $\text{HCO}_3^-$  occurs. However, there is low significant difference between algae and duckweed against the  $\text{HCO}_3^-$  reduction in

**Table 4.2 Mean of anions concentration in the untreated water from polluted Tanjaro River and during the algae and duckweed experiment**

Treatment	Harvesting Frequency (Cultivation period/day)	$\text{HCO}_3^-$	$\text{CO}_3^{2-}$	$\text{Cl}^-$	$\text{NO}_3^{2-}$	$\text{PO}_4^{3-}$	$\text{SO}_4^{2-}$
		mg L <sup>-1</sup>					
Untreated water	Before cultivation (Zero day)	245.91	27.81	84.05	26.86	6.63	94.57
Algae	harvest 1 (5 day)	129.02	29.01	74.72	8.44	2.74	96.52
	harvest 2 (10 day)	88.02	41.27	70.12	8.83	2.63	90.30
	harvest 3 (15 day)	72.56	44.07	79.92	0.04	2.98	100.45
Duckweed	harvest 1 (5 day)	78.26	9.78	67.06	6.07	1.71	86.20
	harvest 2 (10 day)	58.65	4.97	80.81	15.44	0.62	95.23
	harvest 3 (15 day)	50.76	5.85	66.30	9.03	0.48	85.43
Recommend Max concentration (FAO, 1985)		500	60	0-30	0-10	0-2	0-20

the period of the experiment (15 days of cultivation). Algae have more effective to  $\text{HCO}_3^-$  reduction in the wastewater from Tanjaro River during 15 days of cultivation (Fig 4.6a), these differences refer to the growth rate of algae is higher than duckweed in 15 days of cultivation. Also DO increase in the algae aquarium more than duckweed (Fig.4.4a) it means that the photosynthesis processes in algae aquarium higher in comparison to duckweed, Amoroso et al. (1998) investigated the up taking of  $\text{HCO}_3^-$  and  $\text{CO}_2$  by microalgae through chloroplast cell, has capacity to transport and capture the inorganic carbon from media. The results shown the

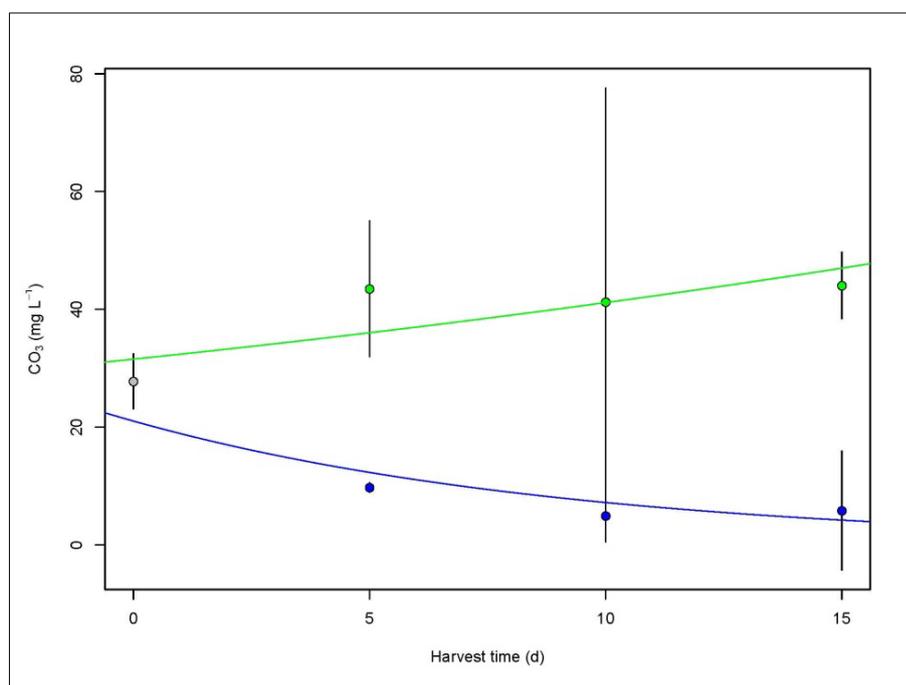
significant difference between untreated water and cultivation time of duckweed Fig (4.6a ) algae shows the significant differences between untreated water sample with 15 day of cultivation, and there is significant difference between algae and duckweed only in 5day of cultivation as shown in Fig (4.6a)



**Figure 4.6a Relationship between  $\text{HCO}_3^-$  concentration in the water sample from Tanjaro River with harvesting time (0, 5, 10, 15) per day, by using non-linear regression function in R, the color illustrated untreated water= gray, algae= green, and duckweed= blue**

The carbonate  $\text{CO}_3^{2-}$  concentrations in the untreated water is ( $27.81\text{mgL}^{-1}$ ) for both algae and duckweed respectively. Carbonate concentration increases in the water sample from Tanjaro River during algae experiment, the maximum concentration was ( $44.07\text{mgL}^{-1}$ ) in the third time of algae biomass harvesting. On the other hand, decreasing in  $\text{CO}_3^{2-}$  concentration recorded throughout duckweed experiment, the untreated water concentration is  $27.81\text{ mg CO}_3^{2-}\text{ L}^{-1}$ , and the minimum value ( $4.97\text{ mg CO}_3^{2-}\text{ L}^{-1}$ ) recorded in the second time of duckweed biomass harvesting (Table 4.2). The results of data analysis in the Fig (4.6 b) showed a most remarkable pattern of relation between the  $\text{CO}_3^{2-}$  concentration and harvesting time, also there is positive relationship between  $\text{CO}_3^{2-}$  concentration and algae harvesting time, in contrast for duckweed showed the negative relation, however, there are the high significant difference between algae and duckweed to  $\text{CO}_3^{2-}$  reduction. In the algae, experiment the concentration of  $\text{CO}_3^{2-}$  was increased, we do not find out the interpretation for this case maybe need more research, on the other hand, in the duckweed experiment decreased. Sun et al. (2016) studied the root exudate

influence the  $\text{CO}_3^{2-}$  equilibrium in the media and maybe duckweed plant through root exudates affected on the  $\text{CO}_3^{2-}$  concentration in the water sample from Tanjaro River.

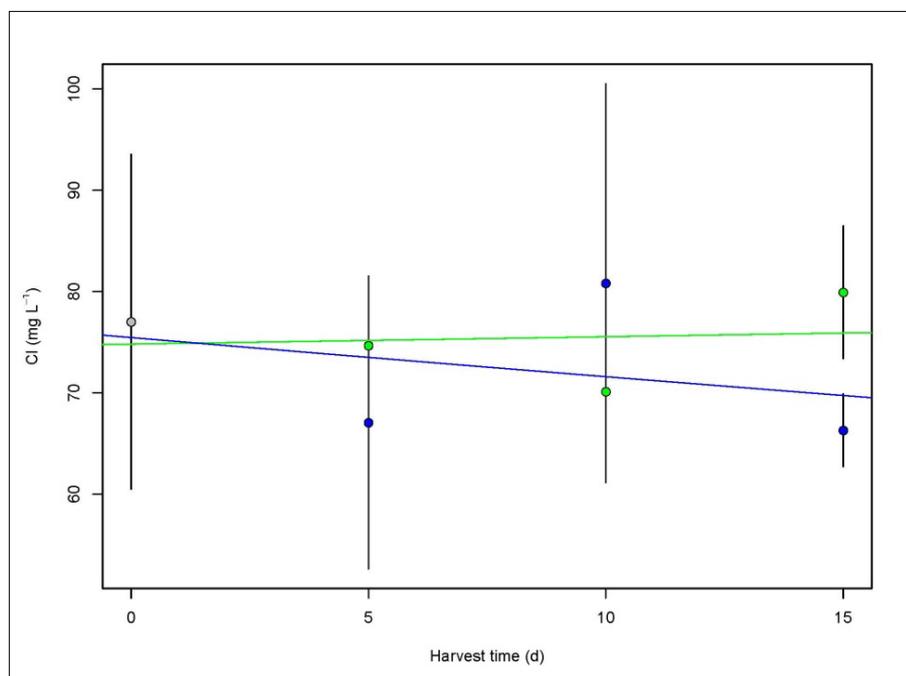


**Figure 4.6 b Relationship between  $\text{CO}_3^{2-}$  concentration in the water sample from Tanjaro River with harvesting time (0, 5, 10, 15) per day, by using non- linear regression function in R, the color illustrated untreated water= gray, algae= green, and duckweed= blue**

#### 4.1.2.2 Chloride ( $\text{Cl}^-$ )

Chloride concentration in the untreated water is ( $84.05 \text{ mg L}^{-1}$ ) for both algae and duckweed respectively, results showed that reduction of the  $\text{Cl}^-$  concentration in the treated water during the time of biomass harvesting for both algae and duckweed aquarium, except third time of algae biomass harvesting (Table 4.2). In addition, the minimum value ( $66.29 \text{ mg Cl}^- \text{ L}^{-1}$ ) recorded in the duckweed experiment. Algae and duckweed efficiency for  $\text{Cl}^-$  reduction during the experiment and harvesting time was revealed that there is negative relationship between  $\text{Cl}^-$  and harvesting time (Fig 4.7), the results explain that increasing of bioremediation time increase of  $\text{Cl}^-$  reduction in the water sample, except the third time of algae biomass harvesting showed unexpected results. However, there is low significant difference between algae and duckweed to reduce the  $\text{Cl}^-$  concentration as shown in Fig (4.7), furthermore duckweed have more efficiency against  $\text{Cl}^-$  reduction in the water sample from Tanjaro River. Results shows agreement with Jahan et al. (2014) they studied the macrophytes and algae to remove the physiochemical characteristic of polluted water and they found 24% of  $\text{Cl}^-$  reduction in the polluted water after treated by aquatic macro/microphytes. Ramirez et al. (2018), they tested

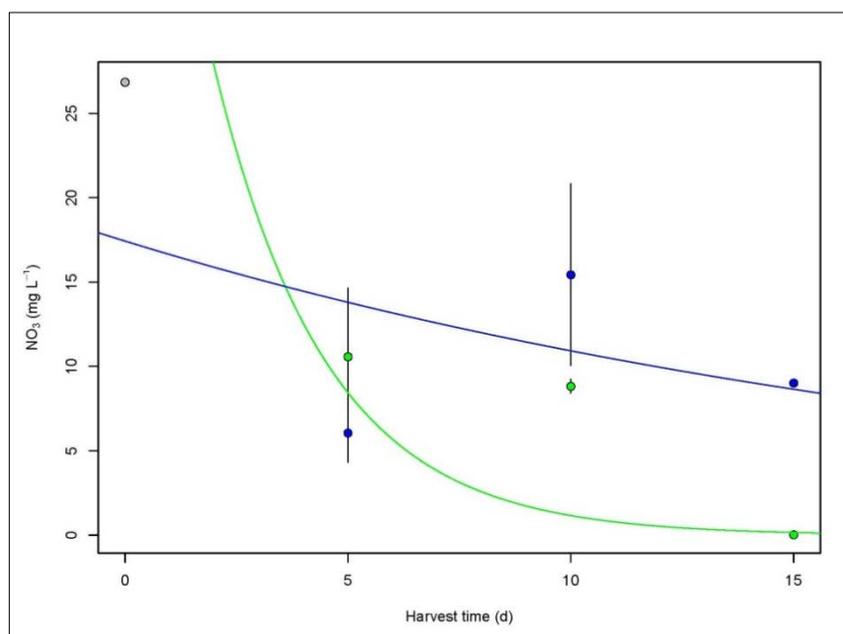
the microalgae efficiency to remove the chloride in the polluted water also found the potential of algae to chloride reduction between 16 to 66% in the 55 days of polluted water sample treatment. The results show non-significant differences between the time of harvesting Fig (4.7).



**Figure 4.7 Relationship between Cl<sup>-</sup> concentration in the water sample from Tanjaro River with harvesting time (0, 5, 10, 15) per day, by using non- linear regression function in R, the color illustrated untreated water water= gray, algae= green, and duckweed= blue**

#### 4.1.2.3 Nitrate (NO<sub>3</sub><sup>-</sup>)

The mean of NO<sub>3</sub><sup>-</sup> value (26.86 mg L<sup>-1</sup>) in the untreated water (Table 4.2), during the experiment the NO<sub>3</sub><sup>-</sup> concentration decreased, minimum value (0.04 mg NO<sub>3</sub><sup>-</sup>L<sup>-1</sup>) recorded in the third time of algae biomass harvesting. However, the relation between nitrate concentration in the water sample and harvesting time of (algae and duckweed biomass) showed the negative relation (Fig.4.9), results explain that instance of increasing harvesting time the NO<sub>3</sub><sup>-</sup>concentration reduce in the water sample from Tanjaro River, besides that there is a significant difference between algae and duckweed to reduce the NO<sub>3</sub><sup>-</sup> concentration (Fig 4.8) especially in 10 and 15 day of harvesting time. In addition, algae have more efficiency to reduce NO<sub>3</sub><sup>-</sup>concentration; Al-Nozaily et al. (2000); Goopy and Murray (2003) concluded the reduction of NO<sub>3</sub><sup>-</sup>in the polluted water by using algae. Although, Porath and Pollock( 1982); Zimmo et al (1995); Muradov et al. (2014) and Rathod (2016) found that; algae and duckweed have the efficiency to remediate NO<sub>3</sub><sup>-</sup> in the polluted water through the bioremediation process. Results from this study are acceptable, due to important of NO<sub>3</sub><sup>-</sup> ion in the metabolism system in the algae and duckweed (Zimmo, 2005).



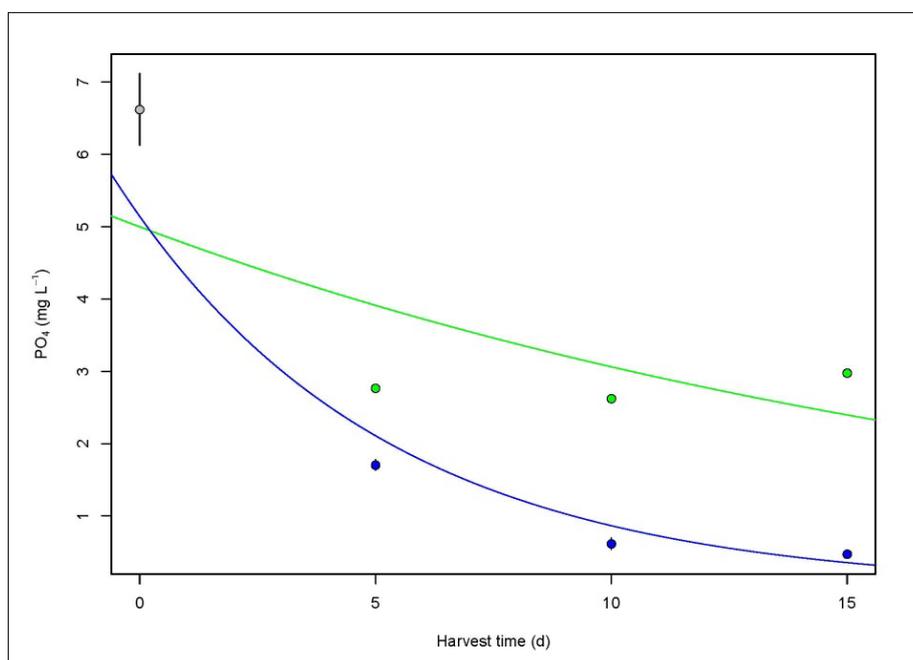
**Figure 4.8** Relationship between  $\text{NO}_3^-$  concentration in the water sample from Tanjaro River with harvesting time (0, 5, 10, 15) per day, by using non-linear regression function in R, the color illustrated untreated water = gray, algae = green, and duckweed = blue

#### 4.1.2.4 Phosphate ( $\text{PO}_4^{3-}$ )

As shown in the Table (4.2)  $\text{PO}_4^{3-}$  concentration in the untreated water from Tanjaro River is ( $6.63 \text{ mg L}^{-1}$ ). During the experiment, the  $\text{PO}_4^{3-}$  concentration reduced as harvesting time increased (cultivation period). The minimum mean value ( $0.48 \text{ mg PO}_4^{3-} \text{ L}^{-1}$ ) recorded in the third time of duckweed biomass harvesting. However, the test for the relationship between  $\text{PO}_4^{3-}$  dependent on harvesting time showed the negative relation (Fig 4.9), which means that by increasing the harvesting time (cultivation period) the reduction of  $\text{PO}_4^{3-}$  concentration increase. In addition, there is a significant difference between algae and duckweed against the  $\text{PO}_4^{3-}$  reduction in 10 and 15 day during the experiment (Fig 4.9), results conclude that the phosphate remediation increased by increasing the bioremediation period, results also indicated that duckweed has more efficiency toward  $\text{PO}_4^{3-}$  removing in the polluted water from Tanjaro River in comparison with algae. Results of the present study showed the agreement with Al-Nozaily et al. (2000); Goopy and Murray (2003); Zimmo (2005) Sekomo et al. (2012); Saikumar et al. (2014) they investigated that algae and duckweed have the ability to remediate the  $\text{PO}_4^{3-}$  in the polluted water. Decreasing of  $\text{PO}_4^{3-}$  concentration refer to the uptake by algae and duckweed as an essential nutrient, it has been used as a source of P ion for the enzymatic process, according to a study by Larsdotter (2006) reduction of  $\text{PO}_4^{3-}$  in the bioremediation, experiment refers to precipitate and adsorption of  $\text{PO}_4^{3-}$  by colloidal and other metalloids in the polluted water.

#### 4.1.2.5 Sulfate ( $\text{SO}_4^{2-}$ )

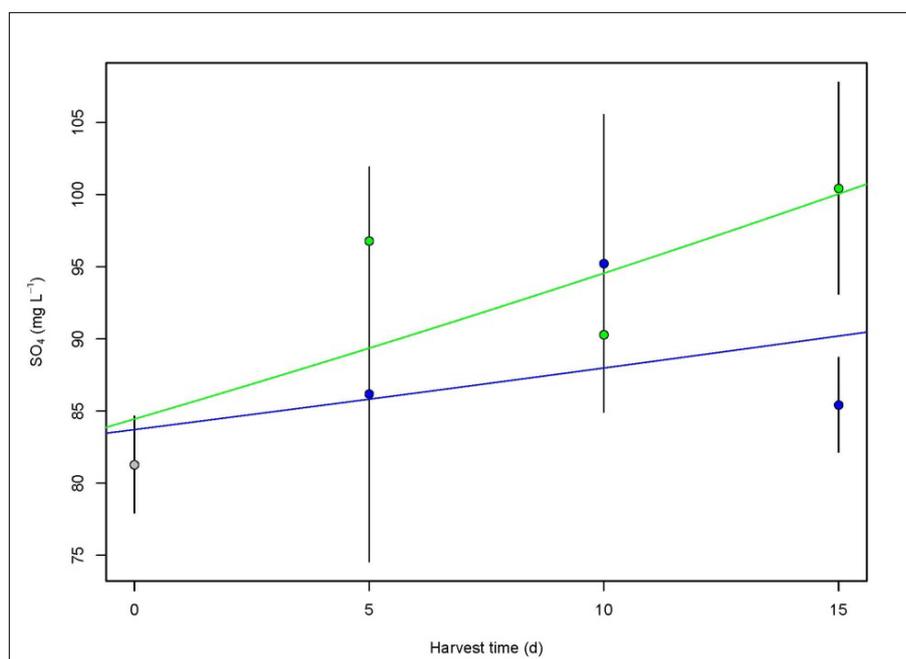
The mean value of  $\text{SO}_4^{2-}$  concentration in the untreated water from Tanjaro River is ( 94.57  $\text{mg SO}_4^{2-} \text{ L}^{-1}$  ) for algae and duckweed respectively, (Table 4.2), although the concentration of  $\text{SO}_4^{2-}$  increased in the algae aquarium, and the maximum mean of value (100.45  $\text{mg SO}_4^{2-} \text{ L}^{-1}$  ) in the third time of algae biomass harvesting (Table 4.2). On the other hand,  $\text{SO}_4^{2-}$  concentration decreased in the duckweed experiment, except for the second time of duckweed biomass harvesting (10 days of cultivation)



**Figure 4.9 Relationship between  $\text{PO}_4^{3-}$  in the water sample from Tanjaro River concentration with harvesting time (0, 5, 10, 15) per day, by using non-linear regression function in R, the color illustrated untreated water water= gray, algae= green, and duckweed= blue**

The minimum value (85.43  $\text{mg SO}_4^{2-} \text{ L}^{-1}$ ) recorded in the third time of duckweed biomass harvesting as shown in the Table (4.2). However, the relation between  $\text{SO}_4^{2-}$  concentrations in the wastewater sample with harvesting time showed the positive relation (Fig.4.10), whereas the results explained that when the harvesting time increase the concentration of  $\text{SO}_4^{2-}$  increases in wastewater, and it is unexpected, although there is non-significant difference between algae and duckweed in  $\text{SO}_4^{2-}$  with harvesting time during the experiment, except 15 day. In addition, the result concludes that the bioremediation of polluted water by algae and duckweed have effect on the  $\text{SO}_4^{2-}$  concentration outline. Results do not show the agreement with the previous research study by Gupta et al. (2015) where they found a reduction of  $\text{SO}_4^{2-}$  in the treated water

by algae and duckweed. Although the results of our study repeated three times during the experiment to find out the solution, may need more research studies.



**Figure 4.10 Relationship between  $\text{SO}_4^{2-}$  in the water sample from Tanjaro River with harvesting time (0, 5, 10, 15) per day, by using non-linear regression function in R, the color illustrated untreated water= gray, algae= green, and duckweed= blue**

### 4.1.3 Cations ( $\text{Ca}^{2+}$ , $\text{Mg}^{2+}$ , $\text{Na}^+$ and $\text{K}^+$ ) concentration in the water sample from Tanjaro River during algae and duckweed experiment

#### 4.1.3.1 Calcium ( $\text{Ca}^{2+}$ ) and Magnesium ( $\text{Mg}^{2+}$ )

Calcium concentration is  $151.33 \text{ mg L}^{-1}$  in the untreated water (Table 4.3), after water treatment by algae and duckweed, the decreasing of  $\text{Ca}^{2+}$  concentration recorded and the minimum mean value ( $28.04 \text{ mg Ca}^{2+} \text{ L}^{-1}$ ) in the second time of algae biomass harvesting. On the other hand, in the duckweed experiment the minimum value ( $28.00 \text{ mg Ca}^{2+} \text{ L}^{-1}$ ) in the third time of duckweed biomass harvesting.

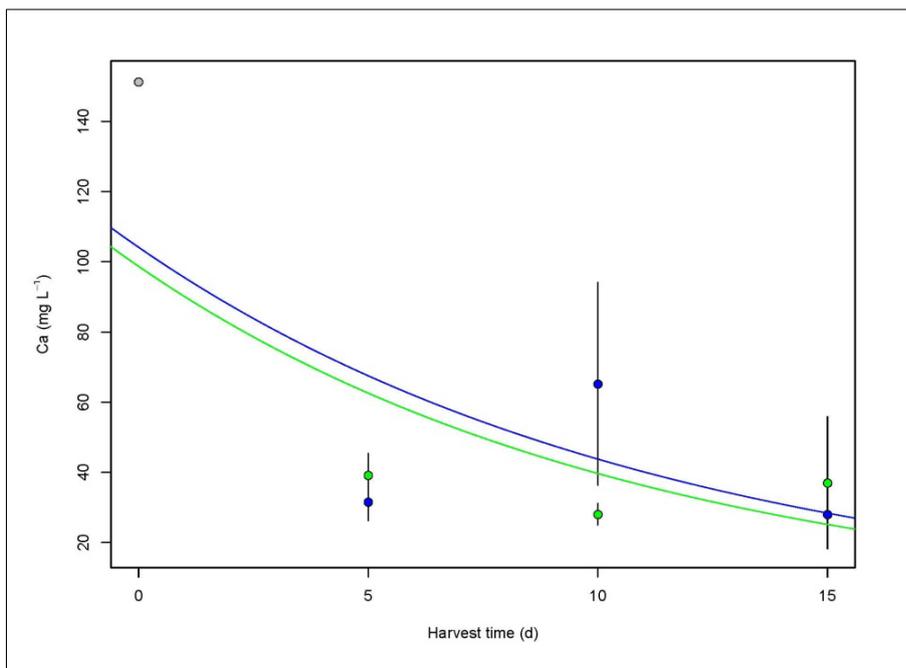
In contrast, with  $\text{Ca}^{2+}$  concentration, the  $\text{Mg}^{2+}$  concentration increased during bioremediation of water sample from Tanjaro River by (algae and duckweed), while  $\text{Mg}^{2+}$  concentration  $11.39 \text{ mg L}^{-1}$  in the untreated water. In addition, the maximum mean value ( $30.58 \text{ mg Mg}^{2+} \text{ L}^{-1}$ ) recorded in the second time of duckweed biomass harvesting. However relationship of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentration in the water sample with harvesting time present in the Fig (4.11 a; b), results showed a negative relationship between  $\text{Ca}^{2+}$  and harvesting time, with significant

differences between untreated water with treated water from 5 day to 15 day of cultivation, but there are non-significant differences between the time of harvesting, which explained that  $\text{Ca}^{2+}$  concentration decreased in water during the period of algae and duckweed cultivation. In addition, there are non-significant differences between algae and duckweed in  $\text{Ca}^{2+}$  reduction during the experiment, except 10 days of harvesting time (Fig 4.11a). Furthermore, results in the present study showed that algae and duckweed have the efficiency to reduce the  $\text{Ca}^{2+}$  concentration in the wastewater from Tanjaro River.

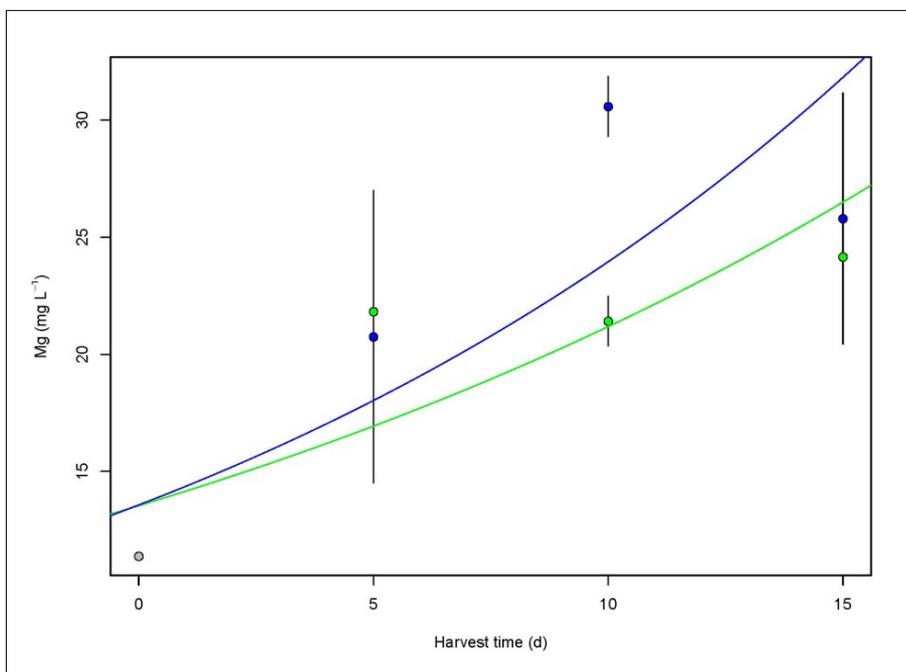
On the other hand, there is a positive relationship between  $\text{Mg}^{2+}$  concentration in the water sample from Tanjaro River and harvesting time (Fig 4.11b), with the non-significant difference between algae and duckweed against  $\text{Mg}^{2+}$  concentration in the water with harvesting time, except 10 days of cultivation showed a significant difference, algae and duckweed have same efficiency pattern on the  $\text{Mg}^{2+}$  concentration in the treated water. The results of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  remediation in the polluted water showed different patterns; algae and duckweed have the efficiency to remove the  $\text{Ca}^{2+}$  concentration in the polluted water in contrast with  $\text{Mg}^{2+}$ . However, the results of the present study agree with Muradov et al. (2014) where they found the reduction of  $\text{Ca}^{2+}$  and they investigated that  $\text{Ca}^{2+}$  ion is second abundance ion for the growth rate of algae and duckweed after NPK concentration in the polluted water. Results of  $\text{Mg}^{2+}$  increasing agree with Krems et al. (2013) they found the replacement of  $\text{Mg}^{2+}$  ion by heavy metal in the chlorophyll particles, also cause the decrease of chlorophyll during the time of experiment for both (algae and duckweed) and increasing the  $\text{Mg}^{2+}$  ion in the medium.

**Table 4.3 Mean of Cation concentration in the untreated water and during the bioremediation experiment by algae and duckweed**

Treatment	Harvesting Frequency (Cultivation/day)	$\text{Ca}^{2+}$	$\text{Mg}^{2+}$	$\text{K}^+$	$\text{Na}^+$
		mg L <sup>-1</sup>			
Untreated water	Before cultivation (Zero day)	151.33	11.39	6.17	69.01
Algae	harvest 1 (5 day)	39.48	21.76	4.29	50.75
	harvest 2 (10 day)	28.04	21.42	3.91	75.69
	harvest 3 (15 day)	37.00	24.16	2.78	74.70
Duckweed	harvest 1 (5 day)	31.57	20.75	3.16	79.86
	harvest 2 (10 day)	65.21	30.58	2.70	77.51
	harvest 3 (15 day)	28.00	25.80	2.78	77.62
Recommend Max concentration (FAO, 1985)		0-2	0-5	0.2	0.40



**Figure 4.11a** Relationship between  $\text{Ca}^{2+}$  concentration in the water sample from Tanjaro River with harvesting time (0, 5, 10, 15 ) per day, by using non-linear regression function in R, the color illustrated untreated water= gray, algae= green, and duckweed= blue



**Figure 4.11b** Relationship between  $\text{Mg}^{2+}$  concentration in the water sample from Tanjaro River with harvesting time (0, 5, 10, 15) per day, by using non-linear regression function in R, the color illustrated untreated water= gray, algae= green, and duckweed= blue

#### 4.1.3.2 Potassium ( $K^+$ ) and Sodium ( $Na^+$ )

Potassium concentration is ( $6.17 \text{ mgL}^{-1}$ ) in the untreated water (Table 4.3), the concentration decreased during algae and duckweed experiment. In addition, the minimum mean value ( $2.78 \text{ mg K}^+ \text{ L}^{-1}$ ) recorded in the third time of algae and duckweed biomass harvesting. On the other hand,  $Na^+$  concentration increased in the water sample during bioremediation within algae and duckweed experiment, then the value gradually decreased after the second time of harvesting. However, there are negative relation between  $K^+$  concentration in the water sample from Tanjaro River and harvesting time as shows in the Fig (4.12a), which explain that by increasing of bioremediation time increase the  $K^+$  reduction in the polluted water, although there are non-significant differences between algae and duckweed efficiency to remediate the  $K^+$  concentration in the water sample during bioremediation experiment (Fig 4.12a). Results of  $K^+$  reduction by algae and duckweed are acceptable because  $K^+$  is an essential nutrient for plant growth (Ragel *et al.*, 2019). Contrariwise, there is a positive relationship between  $Na^+$  and harvesting time during algae and duckweed experiment (Fig4.12b) may be during selectivity of algae and duckweed against one valence ion and prefer  $K^+$  ion more than  $Na^+$ , also during ion electrolyte in the cell membranes, the proteins was transport  $Na^+$  in the cell membranes of living organisms, called the glucose symporter, uses the 'sodium gradient to power glucose movement into the cell. Sodium and glucose both move into the cell. Water passively follows the sodium. To restore balance' during the  $Na^+$  and  $K^+$  pump transfers  $Na^+$  back to the extracellular fluid and water follows. In the every cycle of the  $Na^+$  -  $K^+$  pump involves the drive of three  $Na^+$  ions out of a cell, in exchange for two  $K^+$  ions into a cell to maintain charge neutrality on the outside of cells every  $Na^+$  cation is followed by a chloride anion, this neutrality inside the cell of both algae and duckweed cause to increase  $Na^+$  in the water and decrease  $K^+$  (Kay, 2017). There is non-significant difference between algae and duckweed on the  $Na^+$  concentration in the water sample during the experiment, except 5 day. Results shows similarity with El-Kheir *et al.* (2007) concluded the removed of  $K^+$  concentration by duckweed, and  $Na^+$  concentration increasing during the experiment. Furthermore, Muradov *et al.* (2014) investigated the capability of algae to remove  $K^+$  and  $Na^+$  concentration in the polluted water.

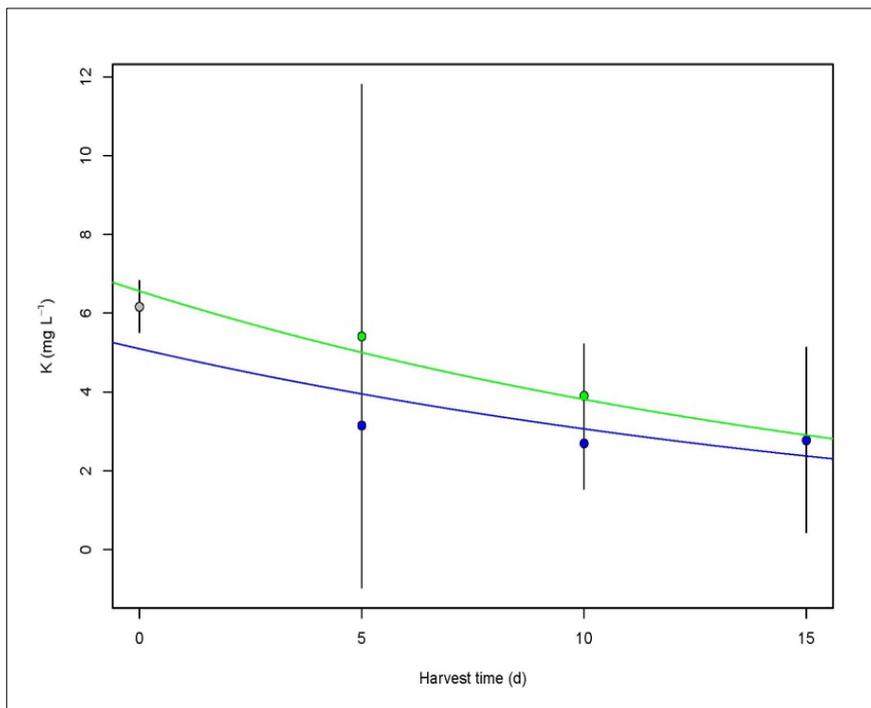


Figure 4.12a Relationship between  $K^+$  concentration in the water sample from Tanjaro River wastewater with harvesting time (0, 5, 10, 15) per day, by using non-linear regression function in R, the color illustrated untreated water = gray, algae = green, and duckweed = blue

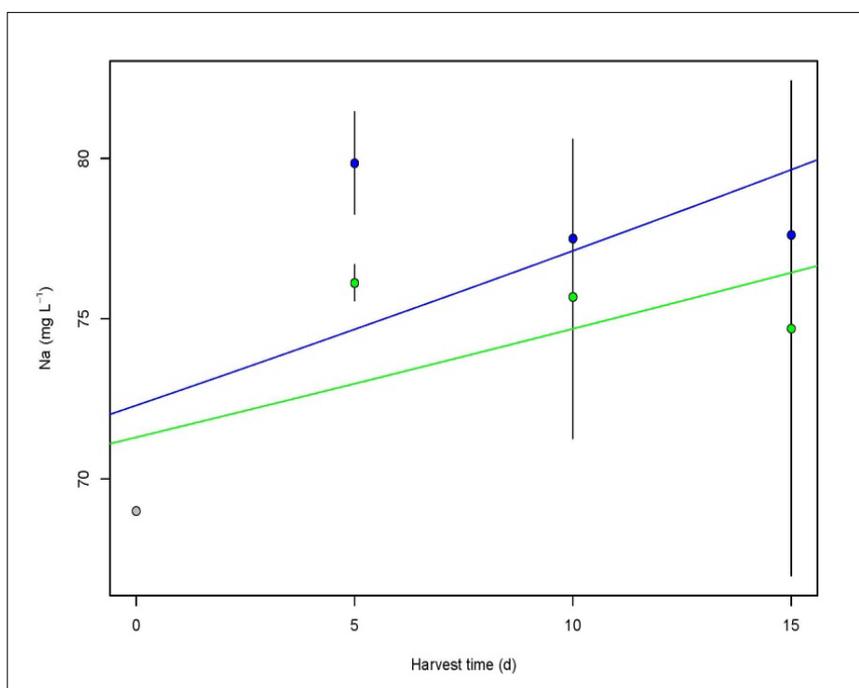


Figure 4.12b Relationship between  $Na^+$  concentration in the water sample from Tanjaro River with harvesting time (0, 5, 10, 15) per day, by using non-linear regression function in R with spearman test, the color illustrated untreated water = gray, algae = green, and duckweed = blue

#### **4.1.4 Heavy metal (Fe, Co, Cd, Pb, Cr, As, Cu, Zn, Mn) concentration in the water sample from Tanjaro River during algae and duckweed experiment**

##### **4.1.4.1 Iron (Fe)**

The Fe concentration ( $93 \mu\text{g L}^{-1}$ ) in the untreated water ( Table 4.4), and after water treating by algae and duckweed the Fe concentration was decreased, in the algae aquarium after 5 days of algae cultivation Fe value ( $0.00 \mu\text{g L}^{-1}$ ) recorded and continues of undetectable Fe in the 10 and 15 days. On the other hand, undetectable of Fe concentration recorded in the 15 days 3-time of duckweed biomass harvesting. The results showed that algae have capacity to remove and uptake  $93 \mu\text{g Fe L}^{-1}$  in the 5 day of cultivation in comparison to the duckweed need 15 day to remove the same concentration. The Zhou et al. (2016) discussed the Fe as an important micronutrient for algae growth rate and have an important role in physiological metabolism and the enzymatic reaction of algae. In addition, Fe concentration use as micronutrient by duckweed (Hasan and Rina, 2009), but the slowest removing than the algae refer to the growth rate of duckweed, was algae faster growing than duckweed in the aquarium in the 15 days of cultivation. Also may refer to the surface area of algae were algae have more surface area to uptake the Fe concentration faster. The results in the Fig (4.13a) showed the negative relation between Fe concentration and time of harvesting during 15 days of cultivation for both (algae and duckweed) also there are significant differences between algae and duckweed to remove Fe concentration in the water especially in the 5 days of biomass harvesting. Nevertheless, after 10 days of biomass harvesting there are non-significant differences between algae and duckweed to removing Fe in the water sample from Tanjaro River. The result concluded; the Fe concentration decreasing by increasing the time of experiment and cultivation.

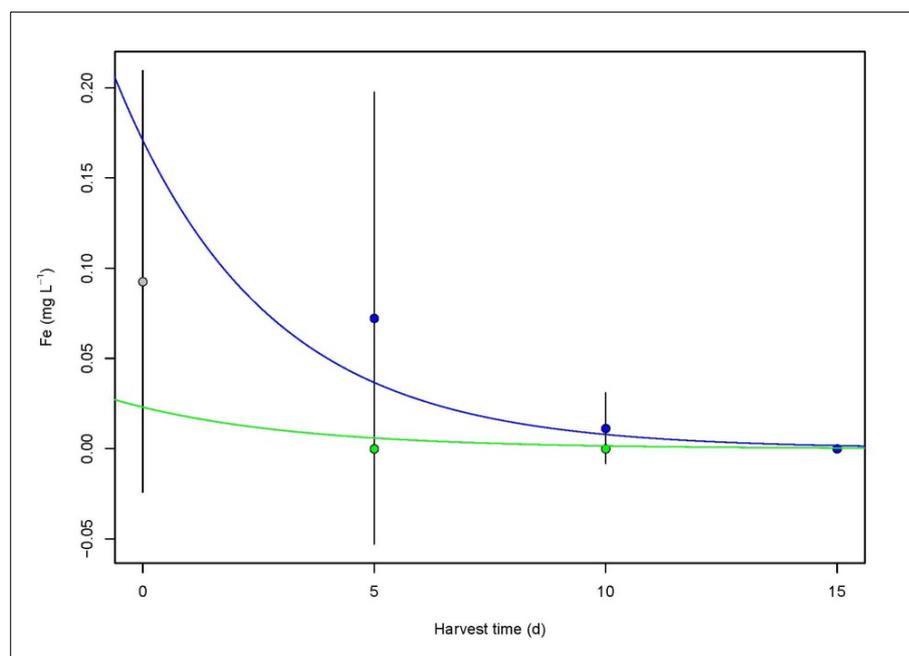
**Table 4.4 Heavy metals concentration ( $\mu\text{gL}^{-1}$ ) in the water sample from Tanjaro River during the bioremediation experiment by algae and duckweed**

Treatment	Harvesting Frequency (cultivation period)	Fe	Co	Cd	Pb	Cr	As	Cu	Zn	Mn
		$\mu\text{gL}^{-1}$								
Untreated water	Before cultivation (zero day)	93.00	22.00	0.33	3.00	8.00	23.00	25.00	1302.00	137.00
Algae	harvest 1 (5 day)	0.00	0.00	0.00	1.00	0.00	21.00	3.00	24.00	36.00
	harvest 2 (10 day)	0.00	0.00	0.00	0.00	0.00	20.00	0.00	13.00	20.00
	harvest 3 (15 day)	0.00	0.00	0.00	0.00	0.00	15.00	0.00	10.00	8.00
Duckweed	harvest 1 (5 day)	72.00	12.00	0.00	0.00	3.00	17.00	15.00	225.00	50.00
	harvest 2 (10 day)	11.00	5.00	0.00	0.00	0.00	17.00	6.00	129.00	46.00
	harvest 3 (15 day)	0.00	1.00	0.00	0.00	0.00	15.00	3.00	13.00	20.00
Recommend Max concentration (FAO, 1985)		5000	50	10	5000	100	100	200	2000	200

#### 4.1.4.2 Cobalt (Co)

The Co concentration in the untreated water is  $22 \mu\text{g L}^{-1}$ , and this value decreased during algae and duckweed experiment (Table. 4.4). The results show decreasing of Co concentration to an undetectable level in the algae aquarium after 5 days of cultivation (first-time) of algae biomass harvesting, it means that algae have capability to remove  $22 \mu\text{g Co L}^{-1}$  in the 5 day of cultivation.

This refers to the maximum growth of algae, which started from 5 days of cultivation and the first pick of chlorophyll *a* was support our finding, was maximum growth started in the 5 days of cultivation. Furthermore, Gulamiourmi and Saeid (2014) studied the Co concentration and there effective of green algae chlorophyll pigments were they found the activity of Co concentration for algae pigment (chlorophyll *a*, *b* and total chlorophyll), may this cause the algae take up the Co concentration in the water sample and it most important for polluted water treatment from Co concentration by green algae.

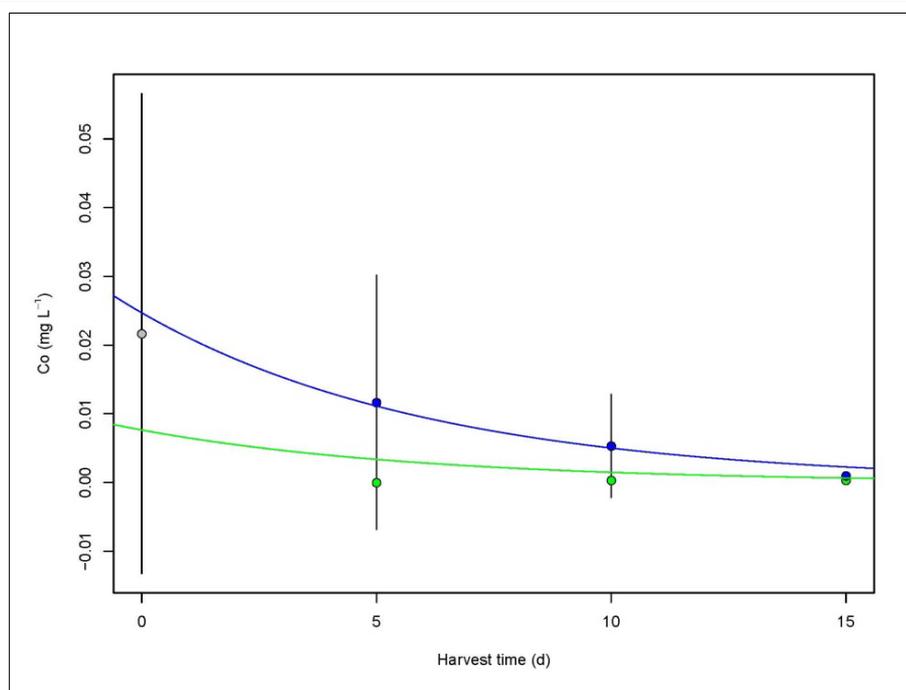


**Figure 4.13a Relationship between Fe concentration in the water sample from Tanjaro River with harvesting time (0, 5, 10, 15) per day, by using non-linear regression function in R, the color illustrated untreated water= gray, algae= green, and duckweed= blue**

On the other hand, duckweed gradually reduced the amount of Co in the water sample during 15 days of cultivation, and the minimum value ( $1 \mu\text{g Co L}^{-1}$ ) in the 15-day cultivation (third time of duckweed biomass harvesting). In addition, Sree et al. (2015) investigated the role of Co concentration in the biosynthesis chlorophyll of duckweed when used for water treatment; also gradually accumulate the Co concentration from the media during 15 days of the experiment; however, Co concentration has the effect of the duckweed plant.

These mechanisms of Co using for photosynthesis and productivity important indication for accumulation and phytoremediation of polluted water by aquatic plant duckweed, the results of the present study conclude the capacity of duckweed to remove Co concentration in the water sample from Tanjaro River.

The results in Fig (4.13b) shows the negative relationship between Co concentrations with harvesting time during 15 days of the experiment. The significantly differences between algae and duckweed to Co reduction in the water sample in 5 days of cultivation (first time of biomass harvesting) were recorded, also by increasing the time of cultivation the capacity of algae and duckweed non-significantly difference are shown (Fig 4.13b). The present results investigated the capacity of both (algae and duckweed) to accumulate and remove the Co from water sample during 15 days of the experiment.



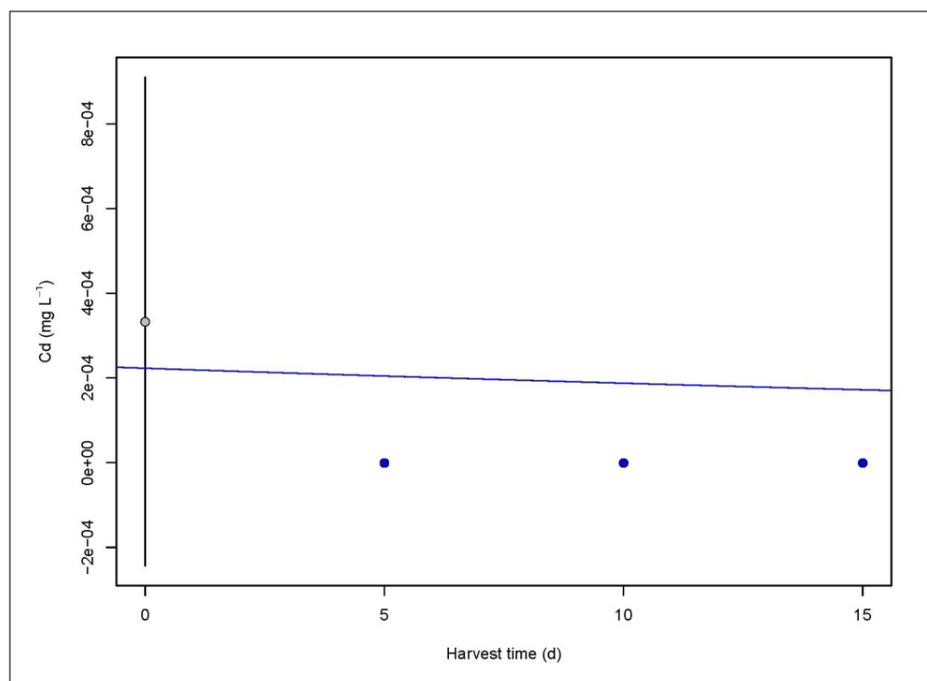
**Figure 4.13b** Relationship between Co concentration in the water sample from Tanjaro River with harvesting time (0, 5, 10, 15) per day, by using non-linear regression function in R, the color illustrated untreated water= gray, algae= green, and duckweed= blue

#### 4.1.4.3 Cadmium (Cd)

Cadmium concentration in the untreated water before cultivation is  $0.33\mu\text{g L}^{-1}$  (Table. 4.4), and this value decreased at the first-time of algae and duckweed biomass harvesting, also the undetectable value of Cd was recorded after 5 days of cultivation (first-time of harvesting) in the both (algae and duckweed) aquarium. The results investigated the ability of algae and duckweed to remove Cd concentration from the Tanjaro River are the same, and the reduction of Cd concentrations high in the both treatment, may refer to the initial concentration of Cd in the water sample from Tanjaro River. The previous studies of Shanab et al. (2012) & Cheng et al. (2016) found the green algae capacity to adaptation in the high concentration Cd in medium, when they study the green algae under different Cd stress. In addition, they found the exposure to algae biological enzymatically system above to  $1\mu\text{g L}^{-1}$ , and also below this value algae use the Cd for photosynthetic mechanisms and pigment production. However, the reduction of the Cd in the algae aquarium has shown agreement with Cheng et al. (2016).

On the other hand, Prasad (2003) study the bioaccumulation of heavy metals especially Cd and Cu in the duckweed plant. In addition, they investigated the physiological response of duckweed to Cd concentration up to ( $10\mu\text{g L}^{-1}$ ), and in the present results, duckweed has ability to remove the Cd from the Tanjaro River water during 5 days of the experiment. The test for

the relation of Cd concentration in the water from Tanjaro River and the duration of the experiment (time of harvesting) showed in the Fig (4.13c), there are non-relation between the Cd concentration and time of (algae and duckweed) biomass harvesting, because of Cd reduction completely in the first time of harvesting. Besides, there are non-significant differences between algae and duckweed to uptake and remove the Cd concentration from water sample. While the results conclude that, algae and duckweed have capability to remediate the Tanjaro River from Cd concentration.



**Figure 4.13c Relationship between Cd concentration in the water sample from Tanjaro River with harvesting time (0, 5, 10, 15 ) per day, by using non-linear regression function in R, the color illustrated untreated water water= gray, algae= green, and duckweed= blue**

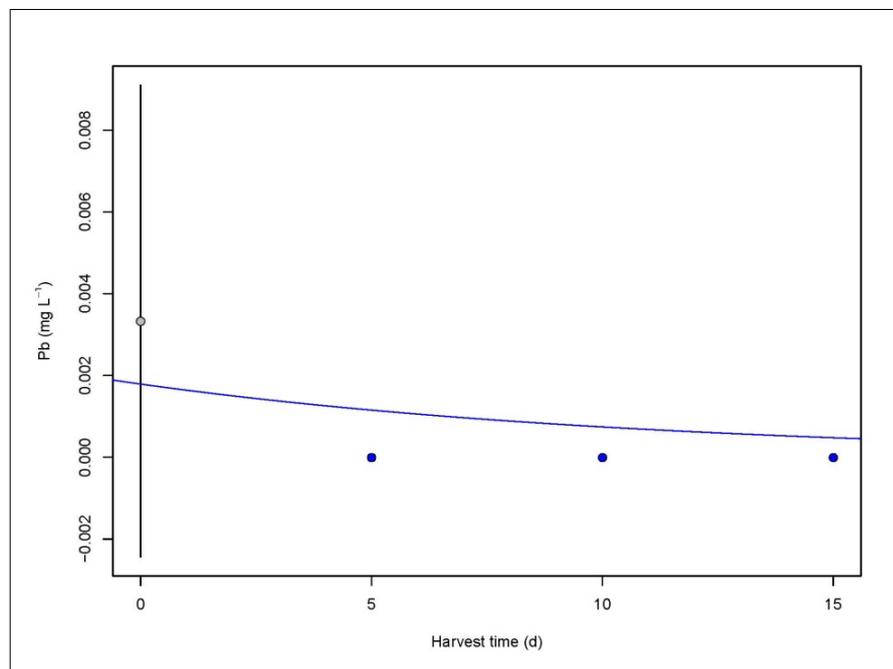
#### 4.1.4.4 Lead (Pb)

The untreated waters from Tanjaro River contain  $3.00 \mu\text{g Pb L}^{-1}$  as shown in the Table (4.4). Moreover, after remediation experiment by algae and duckweed, this value decreased, where the algae reduced the Pb concentration to undetectable value after 10 days of cultivation in comparison to the duckweed, in 5 days of cultivation duckweed has capability to remove Pb completely in the aquarium. Where, duckweed has ability to remove Pb in the water from Tanjaro River more than algae when the time was in countable. The results of the present study in agreement with Verma and Suthar (2015) they found phytoremediation capacity of duckweed to remediate the Pb and Cd in the water under different load of metals (Pb and Cd). Miranda et

al. (2000) they investigated the Lead removable by duckweed in the water under concentration between 30 to 300 mg L<sup>-1</sup>, and during 7 days duckweed recorded maximum growth with capability to remove the metal. While in 13 day of experiment by previous study they point out toxicity occur in the chlorophyll activity, also they concluded up taking of Pb and removing from media have relation with Pb concentration background in the solution.

However, Pb removable by algae from Tanjaro River showed agreement with Shanab et al. (2012), were they found the accumulation and remediation of Pb by microalgae when treated with high concentration of Pb. Moreover, algae have capacity to accumulate Pb in the starch structure with recording high growth rate in chlorophyll and protein in the algae cell under loading of 5-20 mg Pb L<sup>-1</sup>, in our study also we find out the Pb reduction in the 5 day of algae and duckweed cultivation.

The results in Fig(4.13d) showed a negative relation between Pb concentration in the wastewater from Tanjaro River with harvesting time of algae and duckweed, with non-significant differences between algae and duckweed to the reduction of Pb concentration in the aquarium during harvesting time ( 15 days of cultivation). The results concluded that algae and duckweed have ability to accumulate and remove the metal Pb from Tanjaro River very fast during the time of cultivation.



**Figure 4.13d Relationship between Pb concentration in the water sample from Tanjaro River with harvesting time (0, 5, 10, 15) per day, by using non-linear regression function in R, the color illustrated untreated water water= gray, algae=green, and duckweed= blue**

#### 4.1.4.5 Chromium (Cr)

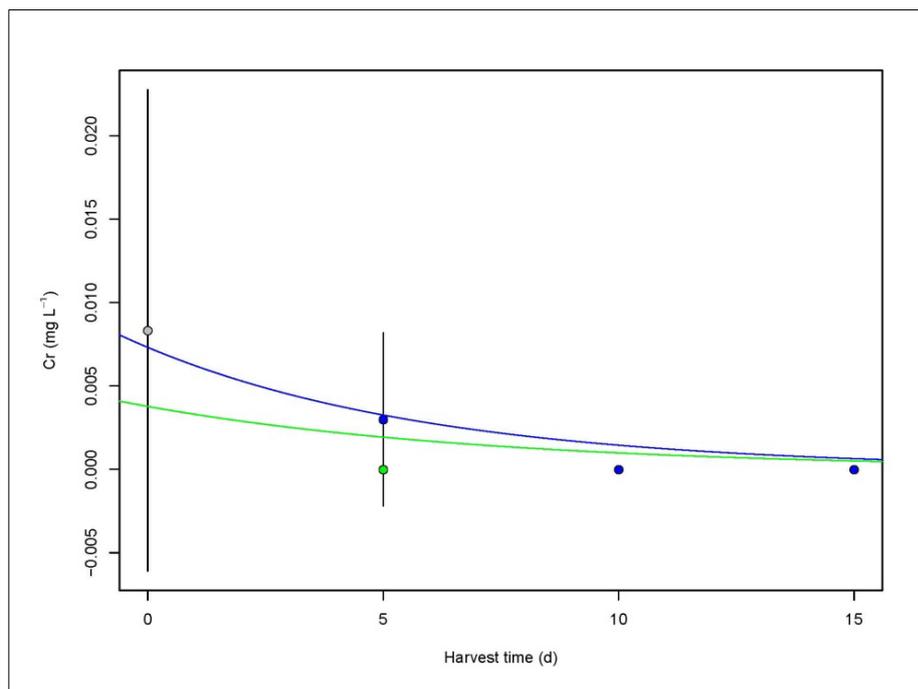
Chromium concentration in the untreated water from Tanjaro River is  $8\mu\text{g Cr L}^{-1}$ , while this value decreased in the water sample after algae and duckweed treatment. Where in the algae aquarium after 5 days of cultivation this value decreased to undetectable value, and in the duckweed aquarium after 10 day of cultivation was the undetectable value of Cr recorded. Up taking of Cr actively by anion carrier or inactively as cation were studied by Volland et al. (2014) they found the computation between iron and Cr as a micronutrient in the solution, when algae have capability to accumulate the (minerals form of Cr) Cr in form of iron-oxygen compound, and localization in the cell wall. However, Ali et al. (2018) were used the dry biomass of green algae as a bio-sorbent to remove the Cr hexavalent in the solution under constant temperature  $45^{\circ}\text{C}$ .

In addition, duckweed have ability to remove Cr in the Tanjaro River in the 10 day cultivation may refer to up taking through duckweed as a micronutrient. Nadiia et al. (2013) found the Cr up taking by duckweed as a form of Cr (VI) and reduction Cr(III) directly in the duckweed cell, also decreasing of Cr concentration in the media depending on the initial concentration, were they found duckweed capability to decrease the Cr concentration in 10 day from ( $50\text{-}200\text{ mg Cr L}^{-1}$ ) to zero value. Moreover, Uysal (2013) found the capacity of duckweed to accumulate the Cr in there biomass in the wide range of pH, and treat the wetland from Cr concentration by duckweed.

The results in Fig (4.13e) showed the negative relation between Cr concentration and time of biomass harvesting of both (algae and duckweed), also non-significant differences between algae and duckweed to remove Cr concentration during the time, except in 5 days of cultivation showed significant differences. Our results investigated reduce of the Cr concentration in the Tanjaro River by algae and duckweed during the time where River treated before using for irrigation.

#### 4.1.4.6 Arsenic (As)

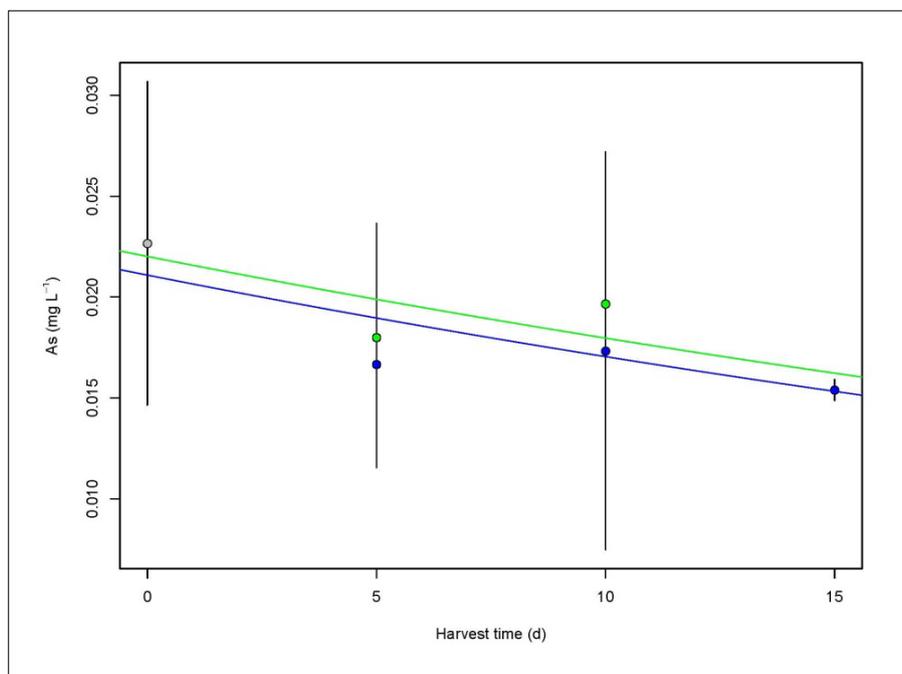
Arsenic concentration in the untreated water is  $23\mu\text{g L}^{-1}$ , and this value decreased to  $15\mu\text{g As L}^{-1}$  in both (algae and duckweed) aquarium for water treatment in the 15 day cultivation. Arsenic is not known as metabolically an essential micronutrient for plant and algae, but up taking and accumulation mechanisms depending on As oxidation state and concentration in the media (Farooq *et al.*, 2016). In addition, Shamsuddoha et al. (2005) studied the accumulation of As by algae and plant with transporting through the food chain.



**Figure 4.13e** Relationship between Cr concentration in the water sample from Tanjaro River with harvesting time (0, 5, 10, 15) per day, by using non-linear regression function in R, the color illustrated untreated water water= gray, algae= green and duckweed= blue

The result in the Fig (4.13f) showed a negative relation between As concentration in the treated water and time of biomass harvesting, also there are non-significant differences between algae and duckweed to As removing in 15 day cultivation, it means that during the period of bioremediation experiment As concentration decrease in the water sample from Tanjaro River.

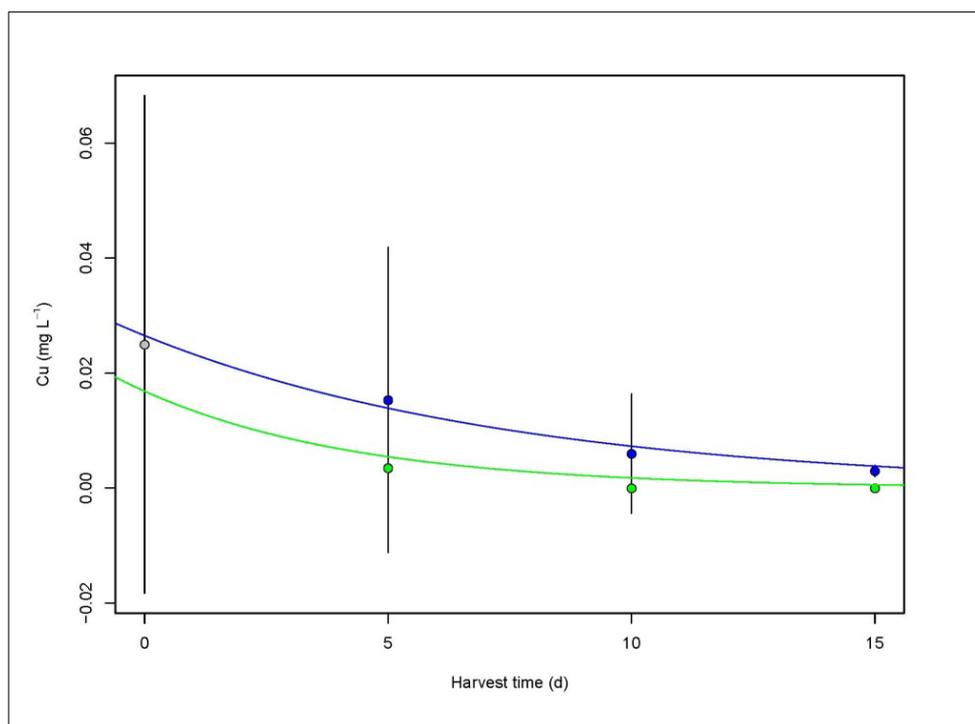
Furthermore, Sandra et al. (2008) found the ability of duckweed to phytoremediation of polluted water from As concentration and accumulation in their biomass, also they investigated to use duckweed as an phyto-remediator plant to treat the polluted water. However, Jasrotia et al. (2014) investigated that algae can be used as phyco-remediator to purify drinking water and capability to bio-sorbet nearly 100% of As concentration in water during 10 days of cultivation.



**Figure 4.13f** Relationship between As concentration in the water sample from Tanjaro River with harvesting time (0, 5, 10, 15) per day, by using non-linear regression function in R, the color illustrated untreated water water= gray, algae= green, and duckweed= blue

#### 4.1.4.7 Cupper (Cu)

The untreated water from Tanjaro River contain of  $25\mu\text{g Cu L}^{-1}$  (Table 4.4), after treatment by algae and duckweed this value was decreased, and in the algae aquarium at 5 days of cultivation  $3\mu\text{g Cu L}^{-1}$ , recorded and in 10 days of algae cultivation were undetectable value of Cu recorded. On the other hand, in the duckweed aquarium, the minimum value ( $3\mu\text{g Cu L}^{-1}$ ) recorded at the end of the experiment at 15 days of duckweed cultivation. The results showed that algae ability to remove Cu from treated water higher than duckweed during the time, and in the 10 days of cultivation reduce the  $25\mu\text{g Cu L}^{-1}$  to undetectable value. Buayam et al. (2019) in their research study found that green microalgae have tolerated capability against Cu in the growth media, investigated the ability of algae to remove more than 80% of Cu, also they found metabolically Cu is an essential micronutrient for algae growth. Also, Ahmad et al. (2020) observed the algae bio-sorption capacity to remove heavy metals include Cu concentration in the polluted water by active and inactive pathways. In addition, they investigated the contact time is very fast to bio-sorption of heavy metals in the media under the alkaline pH and optimal temperature ( $20\text{-}35^{\circ}\text{C}$ ), whereas the removal of heavy metals increases at ( $40\text{-}50^{\circ}\text{C}$ ), it mean that temperature have direct role on the Cu removing by algae also in the our study the water sample temperature between  $22$  to  $27^{\circ}\text{C}$  during the experiment.



**Figure 4.13g Relationship between Cu concentration in the water sample from Tanjaro River with harvesting time (0, 5, 10, 15) per day, by using non-linear regression function in R, the color illustrated untreated water= gray, algae= green and duckweed= blue**

Moreover, Shawqi et al. (2017), found the efficiency of duckweed for pollute water treatment were they compare with tap water as control, and they investigated that duckweed ability to remove 85% of Cu from polluted water in 15 days of the retention period. Also, the Cu used by duckweed as essential micronutrient from water media (Shawqi *et al.*, 2017).

The results in Fig (4.13g) showed the negative relation between Cu concentrations in the water sample with the period of biomass harvesting (15 days), also showed significant differences between algae and duckweed specifically in 5 days of cultivation (biomass harvesting). Wherever results investigated that algae and duckweed have ability to remove Cu concentration in the water from Tanjaro River, especially algae capability to remove in the 5 days of cultivation.

#### 4.1.4.8 Zinc (Zn)

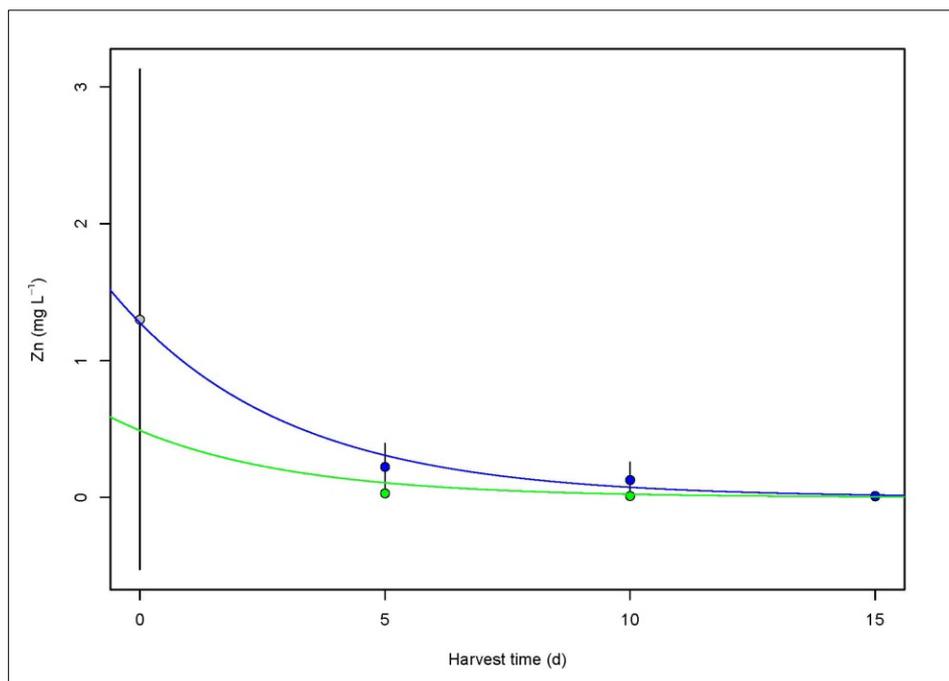
Zinc concentration in the untreated water from Tanjaro River ( $1302\mu\text{L}^{-1}$ ), after treatment by algae and duckweed this value decreased (Table 4.4). In the algae aquarium the minimum value ( $10\mu\text{ZnL}^{-1}$ ) were recorded in the 15 days of algae cultivation, but the pick of reduction of Zn concentrations investigated in the 5 days of algae biomass harvesting (period of cultivation), where the concentration of Zn decreased from 1302 to  $24\mu\text{L}^{-1}$ . Likewise, in the duckweed

treatment minimum value ( $13 \mu\text{g Zn L}^{-1}$ ) recorded in the 15 days of duckweed cultivation. The up taking high amount of Zn concentration by algae and duckweed to refer to the role of Zn as an essential micronutrient to plant and living organisms (Santhanam *et al.*, 2014), also Hojyo and Fukada (2016) studied the role of Zn in immune system in the plant cell against the diseases. Zhou *et al.* (2012) investigated the rapid absorption of Zn concentration in the first day of the green algae bioremediation experiment. However, Heidarpour *et al.* (2019) found the capability of green algae cell to bio-sorption of Zn from contaminating water during 20 days of the experiment also they found the high growth rate of algae when treated by  $100 \text{ mg Zn L}^{-1}$ . In the duckweed, experiment by previous study Allam *et al.* (2015) & Shawqi *et al.* (2017) they studied the duckweed ability to purify the contaminant water also investigated that 85 to 95 % of Zn concentration removed from treated water by duckweed.

The results in Fig (4.13h) showed a negative relation between Zn concentration in the water sample with harvesting time of duckweed and algae, and there are non-significant differences between algae and duckweed to reduce Zn concentrations in the Tanjarao River water during the experiment. Results in the present study investigated that algae and duckweed are good bio-remediation aquatic phyta to reduce the Tanjarao River from excess Zn concentration.

#### 4.1.4.9 Manganese (Mn)

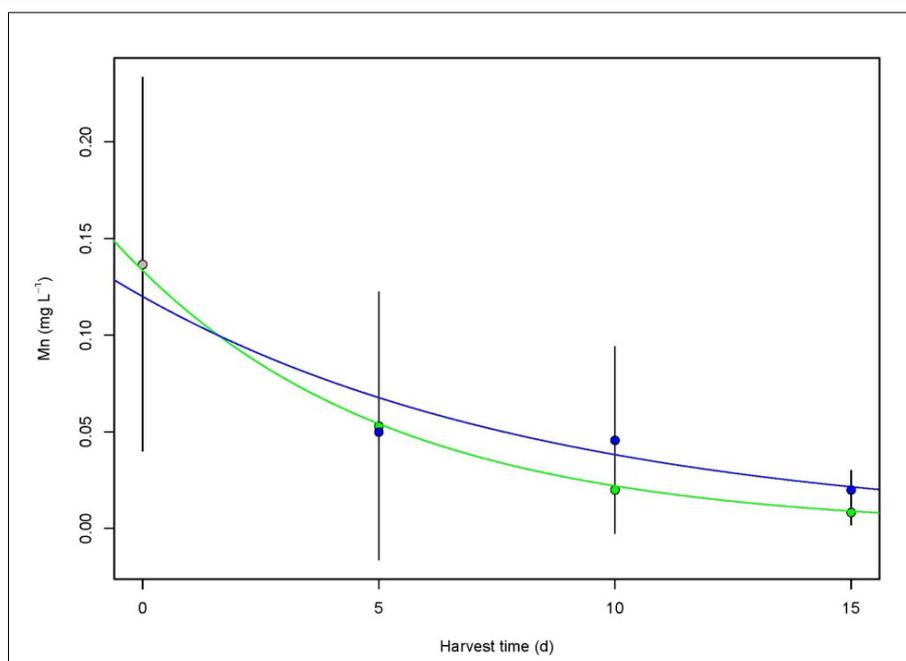
Manganese concentration in the untreated water from Tanjarao River ( $137 \mu\text{L}^{-1}$ ), during the algae and duckweed experiments the concentration of Mn decreased in the water sample Table (4.4), while the minimum mean value ( $8$  and  $20 \mu \text{ Mn L}^{-1}$ ) in algae and duckweed aquarium respectively, and recorded in 15 days of cultivation. The decreasing of Mn concentration is expectable, cause of Mn an essential micronutrient for plant cell, and includes the photosynthesis mechanisms and metabolic role in the plant cell (Alejandro *et al.*, 2020). However, algae removing Mn concentration higher than the duckweed during the time of the experiment. Li *et al.* (2019) investigated the Mn up taking from acid polluted water by microalgae during the indirect oxidation and increasing of pH solution by increasing the dissolved oxygen, and algae have the capability to co-immobilize Mn in the water. Bwapwa *et al.* (2017) treated the acid mine drainage by algae and investigated that algae are good bio-remediator for decreasing the metals concentration in the acid mine drainage and acts as hyper-accumulator with hyper-adsorbent. Furthermore, Yalmaz and Akbulut (2011), studied the effect of duckweed (*Lemna Gibba* and *Lemna Minor*) for polluted water treatment with the ability to remove Cu, Pb, Ni and Mn as a ratio of 57%, 60% 60% and 62% respectively, by *L. Gibba*. In our results, we are found duckweed have the ability to remove 85% of Mn from polluted water of Tanjarao River.



**Figure 4.13h Relationship between Zn concentration in the water sample from Tanjaro River with harvesting time (0, 5, 10, 15) per day, by using non-linear regression function in R, the color illustrated untreated water = gray, algae = green and duckweed = blue**

The results in the Fig (4.13i) show that there are negative relations between Mn concentrations in the water with time of biomass harvesting (15 days of cultivation) in both (algae and duckweed), also there are non-significant differences between algae and duckweed to Mn removing in 5 and 10 days of the experiment. Our present study found that algae and duckweed have ability to reduce the Mn concentration in the Tanjaro River and capacity of algae is more than the duckweed during the 15 days of cultivation.

In general, the concentration of metals decreased during bioremediation experiment, results indicated that by increasing of bioremediation time, influence to reduce the metal concentration in the Tanjaro River water. However, Sekomo et al. (2012) concluded the efficiency of algae and duckweed to remove metals in the polluted water, also Krems et al. (2013) were investigated the requirement of algae and duckweed to metals in the minimum level as a source of micronutrient for growth.



**Figure 4.13i Relationship between Mn concentration in the water sample from Tanjaro River with harvesting time (0, 5, 10, 15) per day, by using non-linear regression function in R, the color illustrated untreated water= gray, algae= green and duckweed= blue**

#### 4.1.5 Metals Removal Efficiency (MRE)

The percentage of metals removal efficiency (MRE) was shown in the Fig (4.14), the efficiency of algae and duckweed is differences to remove specific metals. The results showed that algae high efficiency to remove metals (Co, Cu, Zn and Mn) in the water during experiment in comparison with duckweed (Appendix 4). There is equality between algae and duckweed to remove metals (Fe, Cd, Pb, Cr and As), however the highest value recorded in the (Fe, Cd, Pb, Cr and As), the results conclude that algae and duckweed have high efficiency to remove heavy metals (Fe, Cd, Pb, Cr and As) in the water sample from Tanjaro River. Although El-Kheir et al. (2007) conclude the metals removal percentage by duckweed for eight-day and there are agreements with our finding. Agarwal et al. (2019) summarized the efficiency of algae to purify the polluted water from heavy metals when used as nanoparticle to treat the polluted water. The results in Fig (4.14) shows the harvesting frequency effects on metal removing during experiment, algae 5day of cultivation remove % 100 of metals (Fe, Co, Cd, and Cr), and for Pb maximum value of removing recorded in 10 day of algae harvesting, maximum value of (Zn, Cu, As and Mn) recorded in the 15 day of cultivation. In addition, duckweed remove Cd and Pb completely in the 5 day of harvesting, when remove maximum value of metals (Fe, Co, Cr, Zn, Cu, As, and Mn) in the 15 day of cultivation during course of experiment. In comparison

between algae and duckweed algae faster to remove metals in the water, and duckweed need more time for absorption and accumulating the metals, except in Cd and Pb.

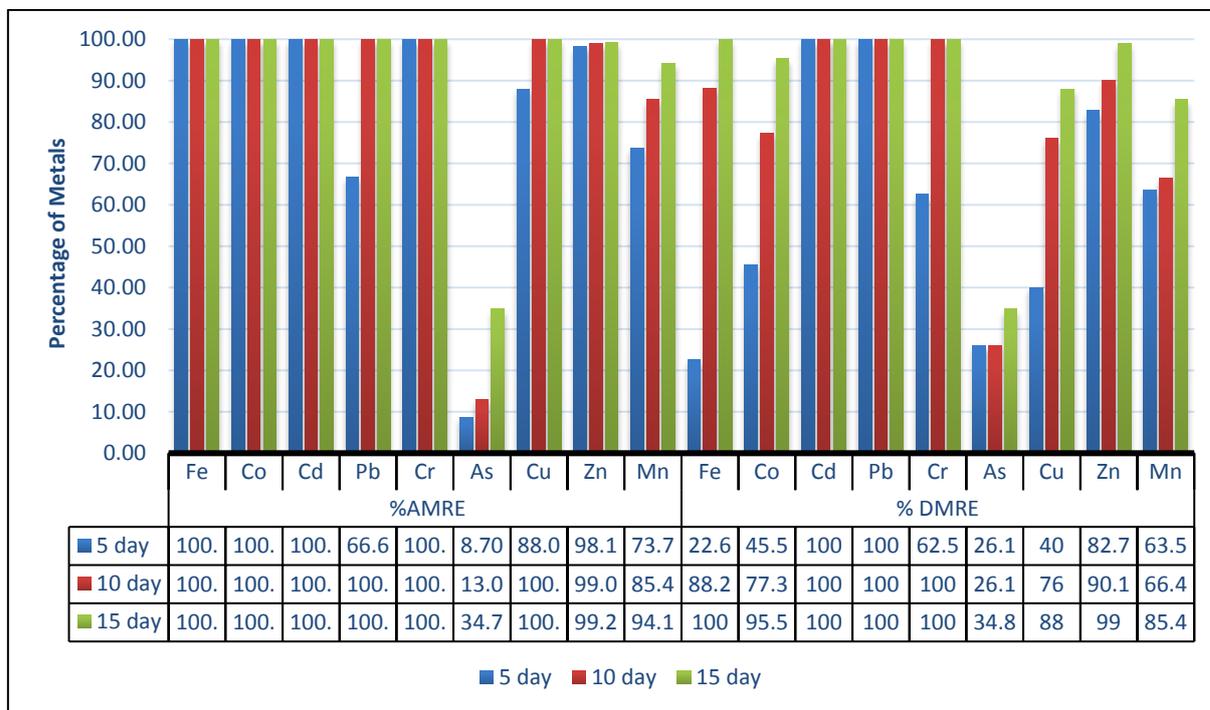


Figure 4.14 Percent of metals removal efficiency by algae and duckweed (AMRE=Algae Metals Removal Efficiency and DMRE= Duckweed Metals Removal Efficiency)

#### 4.1.6 Irrigation Water Quality Index (IWQI) for Tanjaro Rive

Irrigation Water Quality Index of Tanjaro River water sample before and after treated by algae and duckweed were shows in the Fig (4.15). However, the comparison between IWQI of the untreated and treated water sample by algae and duckweed showed a significant increase in value from 12 to 13 under algae treatment during 3-time of harvesting, and result show that algae capability to improve of water in 5 day of cultivation and the value remain the same during experiment for 15 day. In addition, duckweed showed the effects on the IWQI during the experiment for 15 day and higher value (14) of IWQI recorded in the 15 day of cultivation of duckweed. And according to Asadi et al. (2020) classified water quality for irrigation on the three-category depending on suitability for irrigation low<19, medium 19-32, and high >32. Results investigated the improvement in water quality during the experiment, and duckweed ability to improve water for irrigation higher than algae as shows in Fig (4.16). Percentages of improvement by algae 8 % and started from 5 day of algae cultivation and in the 10 and 15 day recorded the same value. Duckweed have ability to improve Tanjaro River water more than algae especially in 15 day of cultivation showed the highest value (17 %) in comparison with 5 and 10 day of cultivation. These results showed agreement with Sekomo et al. (2012) and

Ramirez et al. (2018) who found algae and duckweed have affects to improve the water quality for irrigation.

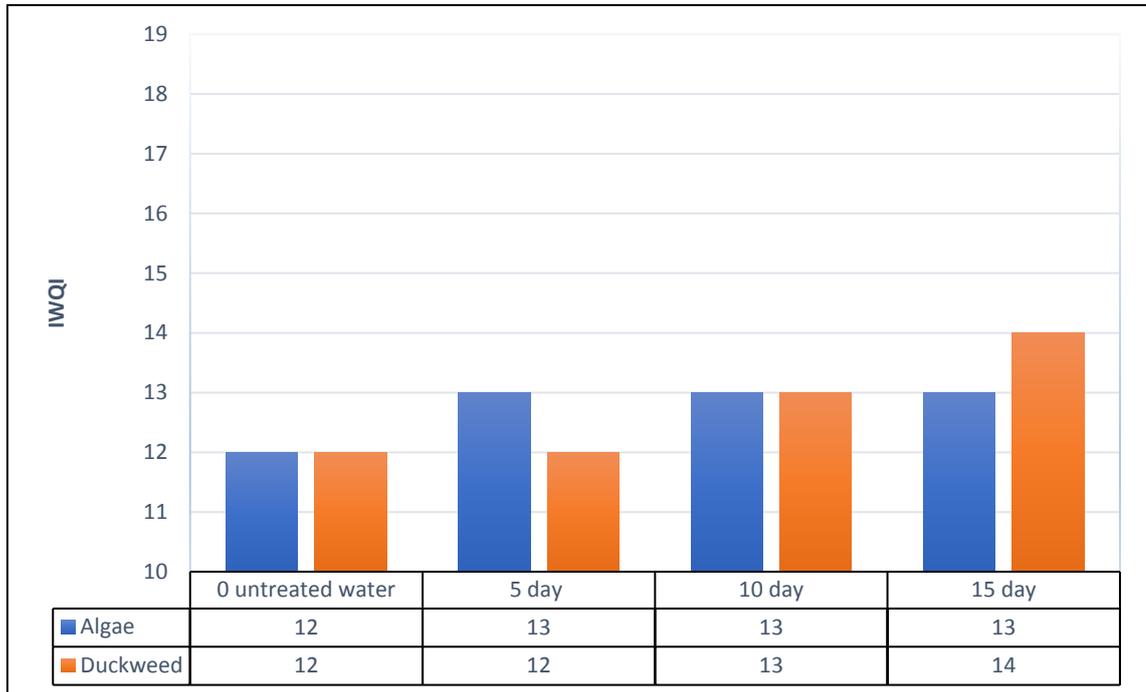


Figure 4.15 Irrigation water quality index (IWQI) of water sample from Tanjaro River and after treated by algae and duckweed during the experiment

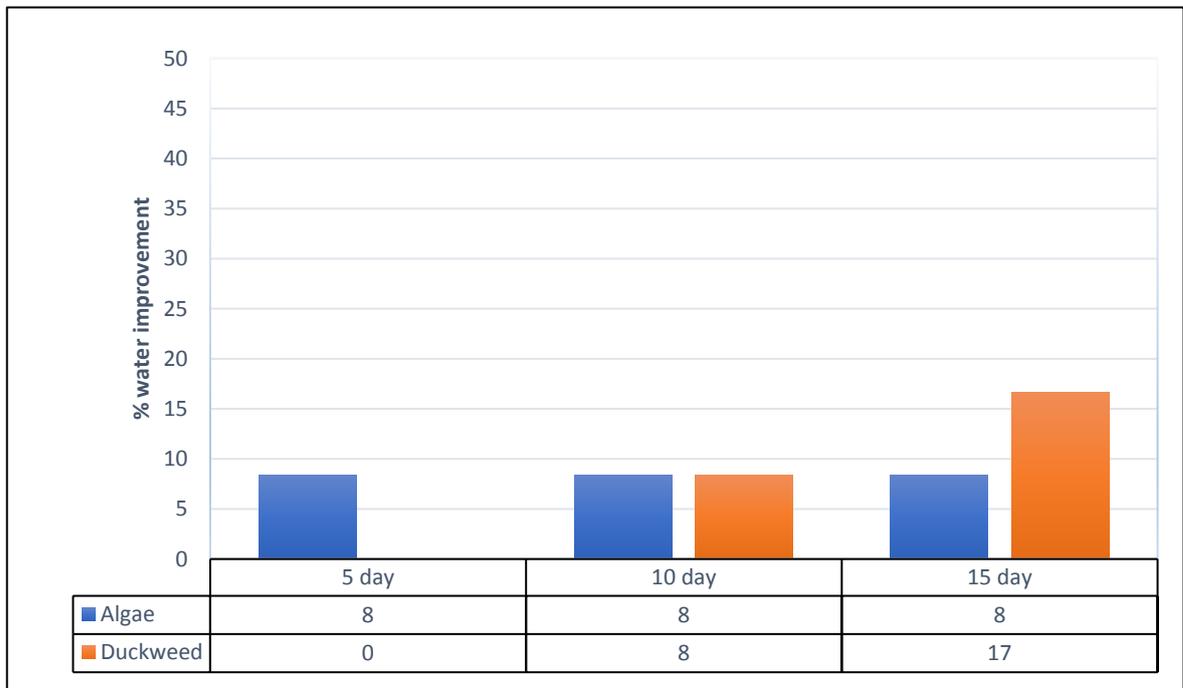


Figure 4.16 Percentages of algae and duckweed capacity to improvement 50 L of water sample from Tanjaro River in 15 day cultivation

#### 4.1.7 Biological Accumulation Factor (Coefficient) for Algae and Duckweed

Plant ability to take up heavy metals from growth media expressed as a ratio of metals concentration in the plant to metals concentration in media. When the value of BAC more than (1), it is mean that plant ability to phytoextraction of metals from media (Yoon et al, 2006; Li et al., 2019). Table (4.5) showed that Algae have the capability to phycoremediate the metals in order (Fe> Mn>Cu>Cr>Co>Zn), also Duckweed have ability to phytoextraction metals (Fe> Cu>Mn>Cr>Co>Zn) On the other hand, Algae and duckweed cannot remediate the metals (As, Pb and Cd) depending on the BAC <1, the Duckweed capacity to heavy metals extraction is more than the Algae.

The results in the present study concluded that; Tanjaro River should be treated by Algae and duckweed before use as a source of irrigated water (Głab and Sowiński, 2019).

**Table 4.5 The Biological Accumulation Coefficient (BAC) of Algae and Duckweed**

Treatment	Fe	Co	Cd	Pb	Cr	As	Cu	Zn	Mn
Algae	1274714.00	466.61	0	0	33338.88	0.00	39663.88	20.13	119056.19
Duckweed	150906.40	10064.17	0	0	29514.35	0.00	142870.26	276.22	93697.10

## 4.2 Sorghum Phytoremediation Experiment

This experiment conducted to evaluate the effect of irrigation frequency of Tanjaro River on soil (Bakrajo soil) physiochemical properties, and to study the amount of metals and ions discharged through the soil to ground water during irrigation processes, also to find out the amount of metals and ions accumulated in the plant (Sorghum) biomass.

### 4.2.1 Physiochemical properties variation of a water sample from Tanjaro River used for irrigation during sorghum experiment (August 1, 2018 to October 1, 2018)

#### 4.2.1.1 Heavy metals concentration in the water sample from Tanjaro River used for irrigation during sorghum experiment

The relationship between concentrations of metals (Fe, Co, Cd, Pb, Cr, As, Cu, Zn and Mn) in the water sample from Tnjaro River with the time of sampling during two months showed in the Fig (4.17A). The relationship between (Fe, Co, Cd, Pb, Cr, As and Zn) concentration and time of sampling remain near steadiness negative during the time of sampling from Tanjaro River in August to October 2018. Results do not show the variation in metals (Fe, Co, Cd, Pb,

Cr, As and Zn) concentration during the experiment with the time of sampling, except in August they had the outline point of metals concentrations in the time of sampling from Tanjaro River. Also, Fe has 3-outline point of concentration in August and first of October during sampling for irrigation. According to Nigar et al. (2012), they studied concentration of metals in the Tanjaro River, they found a variation of metals concentration in the River due to sewages from Sulaymaniyah city.

On the other hand, Mn concentration showed a variable point of value during sampling and irrigation time, Mn has a positive relation with time of sampling (Fig 4.17B). Results conclude that there is decreasing of metals (Fe, Co, Cd, Pb, Cr, As, Cu, Zn) concentration in the wastewater sample during the irrigation time, except Mn increased individually. The decreasing of metal concentration refers to sewer composition feeds the Tanjaro River from Sulaymaniyah city and Majid et al, 2018 discussed the seasonal variation of Tanjaro River water.

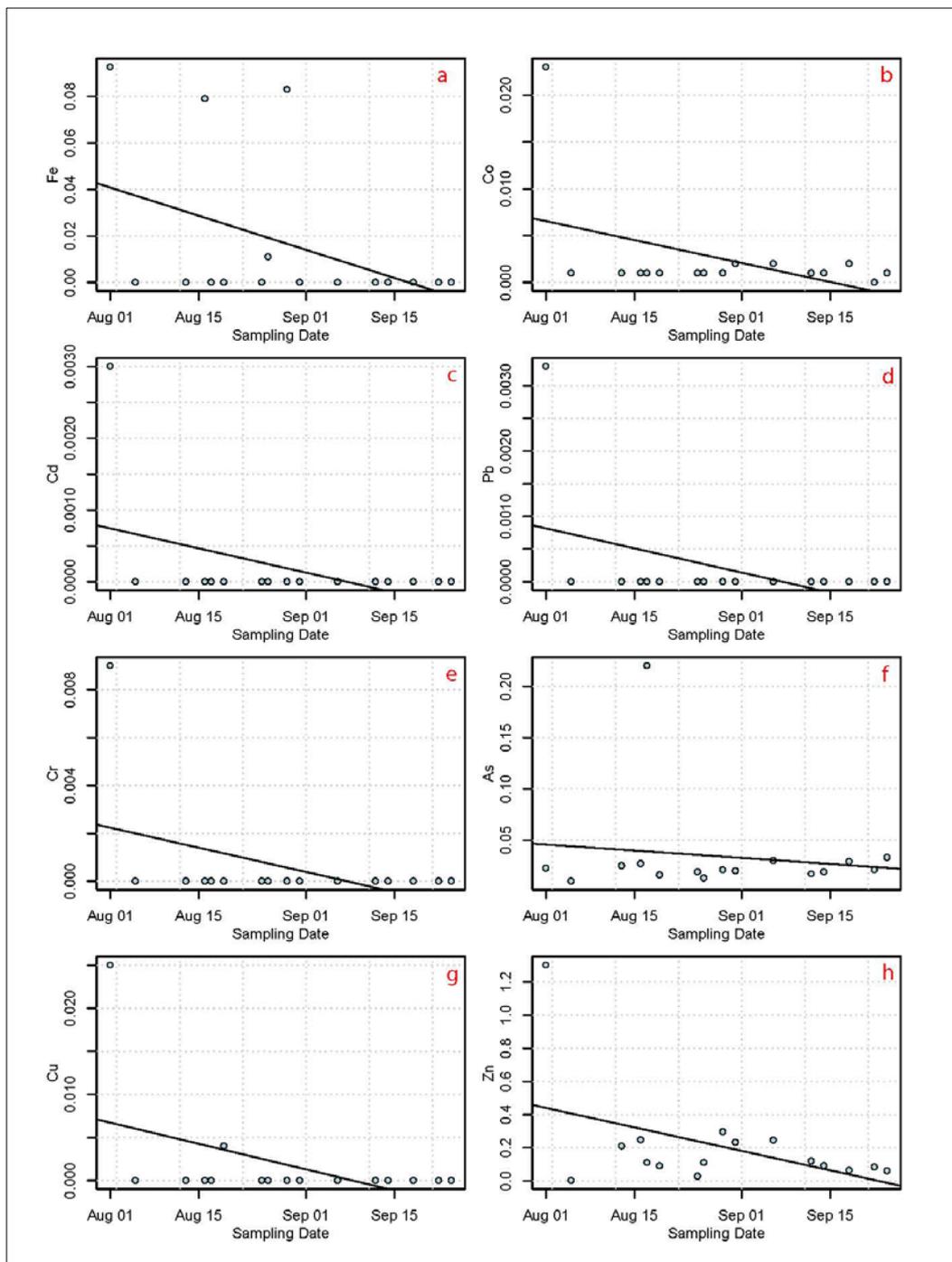
#### **4.2.1.2 Cations ( $\text{Ca}^{2+}$ , $\text{Mg}^{2+}$ , $\text{K}^+$ and $\text{Na}^+$ ) concentration in the water sample from Tanjaro River used for irrigation during sorghum experiment**

Results of cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$  and  $\text{Na}^+$ ) Concentrations in the water from Tanjaro River were used for irrigation showed in the Fig (4.17B). There is a negative relation in  $\text{Ca}^{2+}$  and  $\text{K}^+$  with the time of sampling for irrigation, so the value of  $\text{Ca}^{2+}$  was standing value only have two outline point of value, and  $\text{K}^+$  showed the high variables value in sample concentration during irrigation (Fig 4.17B). On the other hand,  $\text{Mg}^{2+}$  and  $\text{Na}^+$  showed a positive relation with time of sampling. There are no interpretations for decreasing and increasing of cations in the irrigation wastewater and only depending on the sewer daily composition and sewage characteristic from the industrial area (Majid *et al.*, 2018).

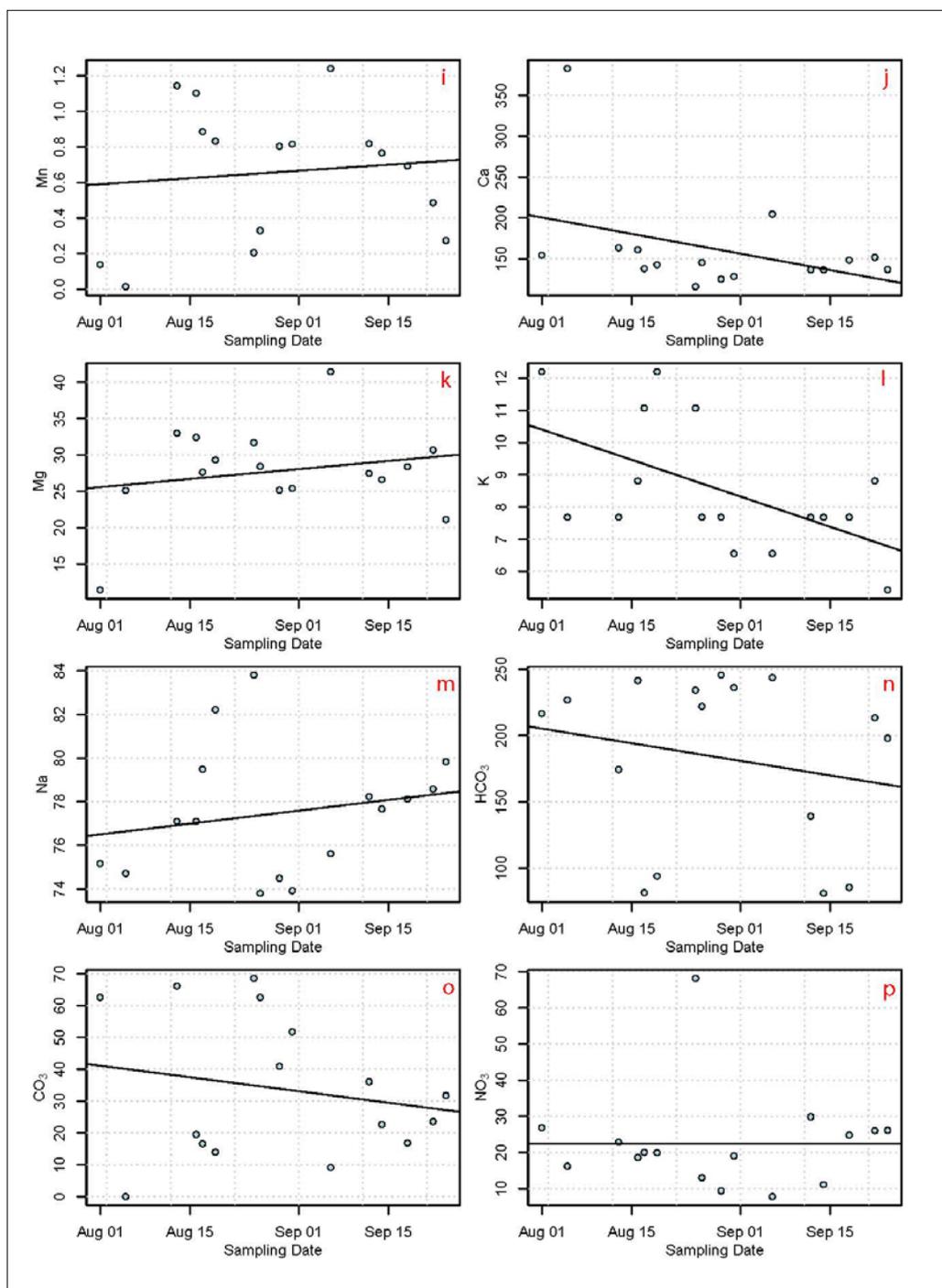
#### **4.2.1.3 Anions ( $\text{HCO}_3^-$ , $\text{CO}_3^{2-}$ , $\text{PO}_4^{3-}$ , $\text{NO}_3^{2-}$ and $\text{SO}_4^{2-}$ ) concentration in the water sample from Tanjaro River used for irrigation during sorghum experiment**

Anion concentrations in the water sample were collected from Tanjaro River during two months of sorghum experiment as showed in the Fig (4.17B;C). There is the negative relation between anion ( $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$  and  $\text{PO}_4^{3-}$ ) concentration with the time of sampling and irrigation from August to October. In addition, the concentration showed variable value separate from the regression line, it means that the concentration of ( $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$  and  $\text{PO}_4^{3-}$ ) decreased during the experiment in the wastewater sample. Nitrate results in the irrigation water sample showed stand line of regression, and there are no relation between the  $\text{NO}_3^{2-}$  concentration and time of sampling, and value of  $\text{NO}_3^{2-}$  rear constant, except at the end of August have one out point of value (Fig. 4.17B).

Results of  $\text{SO}_4^{2-}$  concentration in the irrigation water sample showed the positive relation between the  $\text{SO}_4^{2-}$  concentration and time of wastewater sampling from River and there are increasing in  $\text{SO}_4^{2-}$  value; also, there are dissimilar values between the  $\text{SO}_4^{2-}$  concentration and the sampling dates on the regression line (Fig 4.17C).



**Figure 4.17A** Relationship between the metals (Fe, Co, Cd, Pb, Cr, As, Cu, and Zn  $\text{mgL}^{-1}$ ) concentrations in the water sample from Tanjaro River with time of sampling during sorghum experiment (1, August 2018 to 1, October 2018), by using linear regression function in R



**Figure 4.17B** Relationship between Mn, Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup>, HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup> and NO<sub>3</sub><sup>2-</sup> concentrations (mgL<sup>-1</sup>) in the water sample from Tanjaro River with time of sampling during sorghum experiment (1, August 2018 to 1, October 2018), by using linear regression Coefficient function in R

#### **4.2.1.4 Parameters (DO, pH, EC<sub>25°C</sub>, TDS, TC and Turbidity) value in the water sample from Tanjaro River used for irrigation during sorghum experiment**

The DO concentration in the irrigation water sample during the experiment showed in the Fig (4.17C) and there is a negative relationship between time of sampling and concentration of DO, which results concluded that; DO concentration in the Tanjaro River decreased by increasing the time of sampling between August to October, maybe during the algae biomass growth in the Tanjaro River in this time and made the rivers increases in DO.

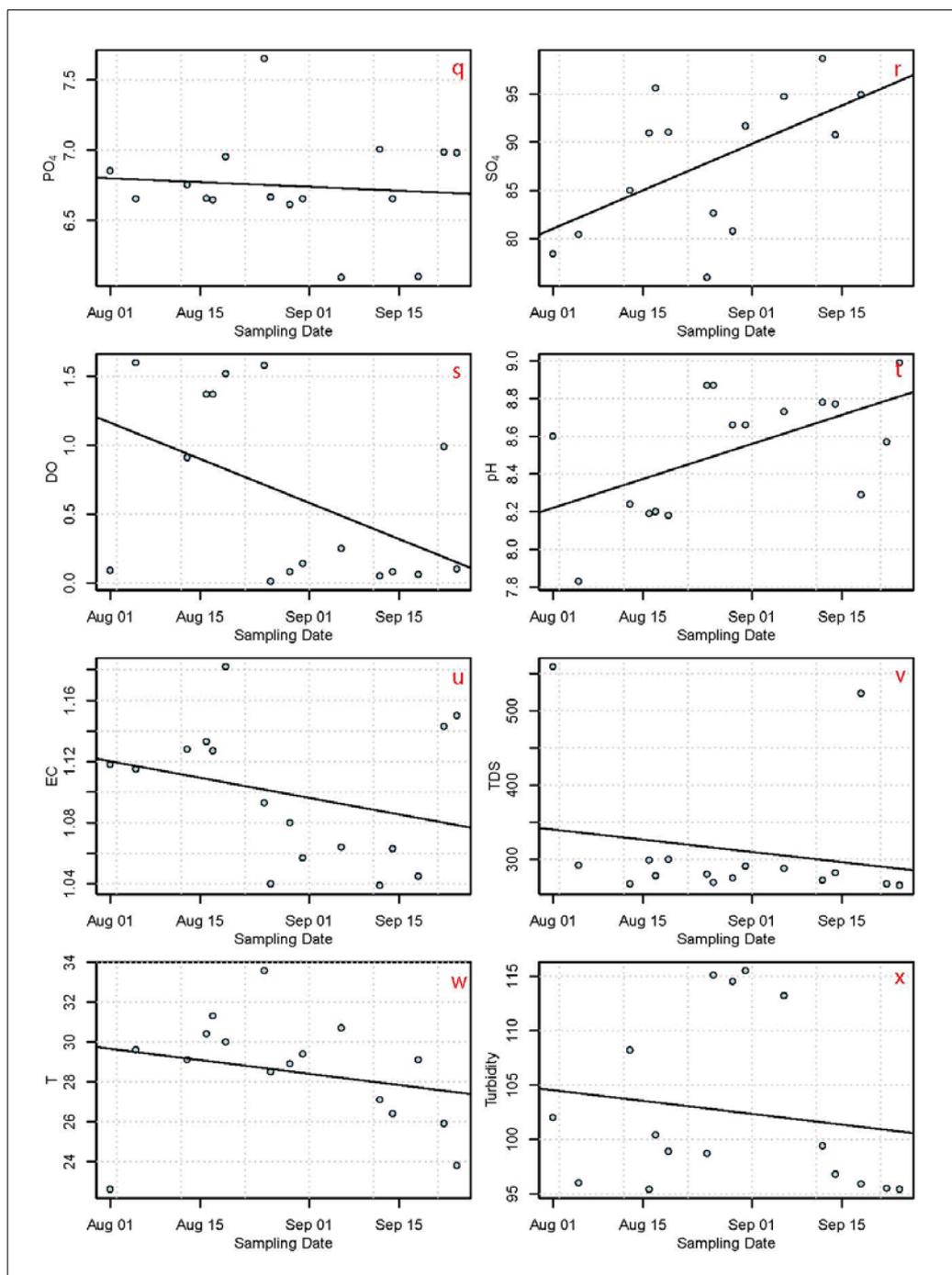
On the other hand, the pH value shows a positive relation with sampling date and the value increased in the time of experiment between Augusts to October. The parameters (T, TDS, Ec and Turbidity) showed the negative relation with time of sampling from Tanjaro River and the values decreased, also the value of Ec and TDS showed constantly point of value on the regression line, only TDS has two outline point in the 1<sup>st</sup>, August and end of September, also Ec has one outline point of value.

The results concluded the variable in the EC and TDS values refers to seasonal changing in the Tanjaro River, or may be due to industrial activity on the side of Tanjaro River.

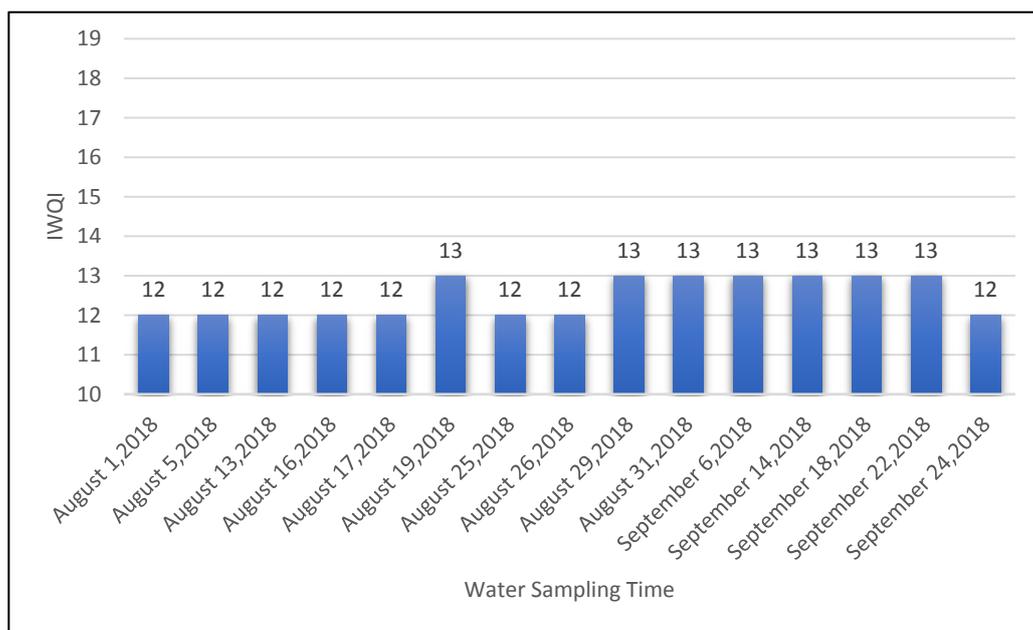
Generally, the results of irrigation water concluded that sampling water from Tanjaro River showed the variable in value in all measurements. In addition, the physiochemical measurements in the irrigation water from Tanjaro River investigated the variation of value in August and September, this variation refers to the swage composition from the city. According to Rasheed et al. (2017) found the pollution in the Tanjaro River by sewer pollutant with health problem surround the Tanjaro area during seasonal sampling, and Rashid, (2010) found the variation in metals and ion concentration seasonally in the Tanjaro River.

#### **4.2.1.5 Irrigation water quality index (IWQI) of Tanjaro River water during sampling time**

The results of IWQI of Tanjaro River water shown in the Fig (4.17E) and the value between (12 to 13), August sampling time recorded value 12 of IWQI except, August 19, 2018. And in the September the quality of water improved naturally during time September except September 24, 2028. The changing quality due to algae growth naturally in the River especially in the sampling location when the temperature and light prefer during day time. our results find out the best time for collection water from River and using it for irrigation.



**Figure 4.17C** Relationship between ( $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ , DO, pH,  $\text{EC}_{25^\circ\text{C}}$ , TDS, TC and Turbidity) concentrations in the water sample from Tanjaro River with time of sampling during sorghum experiment (1, August 2018 to 1, October 2018), by using linear regression Coefficient function in R



**4.17E IWQI of Tanjaro River water sampling during the sorghum experiment**

## **4.2.2 Effect of irrigation frequency on the metals and ion discharging through the soil pots**

### **4.2.2.1 Metals (Fe, Co, Cd, Pb, Cr, As, Cu, Zn and Mn) concentrations in the discharging water from soil pots**

The irrigation frequency; one-time per week (A), two-times per week (B) and three-times per week (C) at the end of the experiment different patterns were shown depending on the solubility of the metals. While the results in the Table (4.6) showed Fe discharged from the soil in order; Control > A > C > B. It means that amount of Fe was discharged in the control higher than other treatment, because of no plant in the pot to uptake the Fe ion, according to Mehes-Smith et al. (2014) investigated the uptaking of metal by the plant when grown in the soil rich of heavy metals. Also, depending on the Fe solubility, the one-time per week of irrigation take the first order, and amount of Fe concentration increase in the solubility and discharged in the three-time per week of irrigation. Also, Rajmohan et al. (2014) found the distribution of Fe metals through the soil profile.

However, in the result in the Table (4.6) subtract the value of Fe that discharging from control with the value of Fe that discharging from all treatments showed negative relation (Fig 4.18a), and there are non-significant difference between 1 time/ week, 2 times/ week and 3 times/ week from week 1 to week 5 of experiment and also no significant differences between time of irrigation investigated from week 5 to week 9.

Table 4.6 Mean concentration of heavy metals in discharge water from sorghum soil pots experiment

Treatment	Irrigation Frequency	Fe	Co	Cd	Pb	Cr	As	Cu	Zn	Mn
		mg L <sup>-1</sup>								
A	1/week	0.0524	0.0029	0.0007	0.0000	0.0001	0.0179	0.0114	0.1052	0.1420
B	2/week	0.0257	0.0021	0.0009	0.0015	0.0005	0.0162	0.0071	0.0744	0.0625
C	3/week	0.0401	0.0041	0.0000	0.0015	0.0016	0.0457	0.0165	0.5067	0.0754
Control	1,2,3/week	0.1077	0.0013	0.0000	0.0022	0.0024	0.0428	0.0134	0.0636	0.1197

The results of Co concentration in the discharging water from soil pot showed increasing by irrigation frequency (Table 4.6). The highest value of Co discharging recorded in the three-time per week of irrigation, the results concluded that Co solubility start in the one-time per week of irrigation and the concentration decreased in the two-time per week, reappearance to discharge high concentration in the three-time per week of irrigation in the order C> A> B. The amount of Co in the control was lower than other treatments, its return to the plant root activity on Co

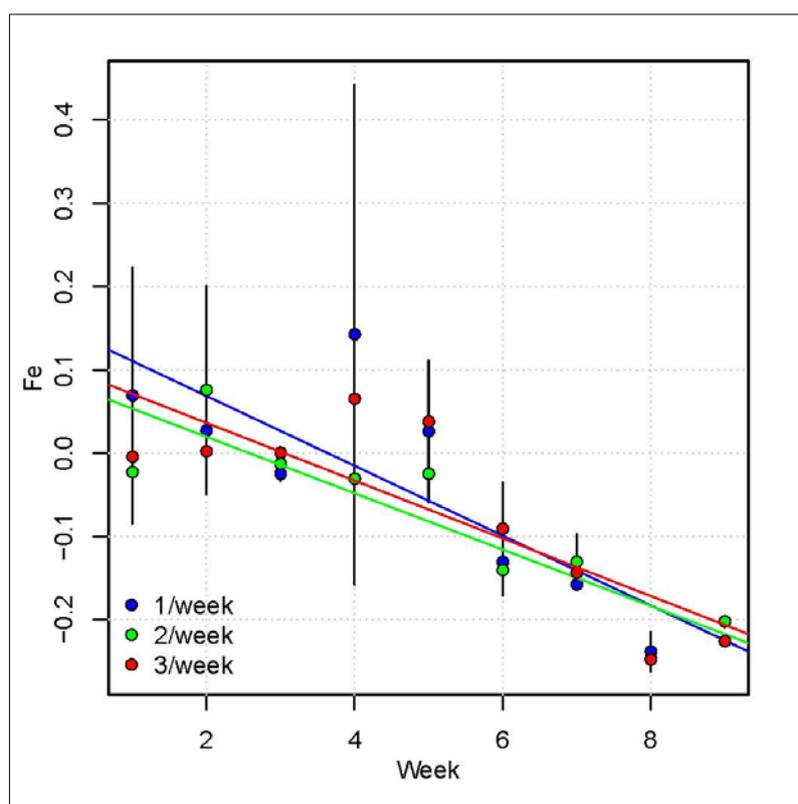
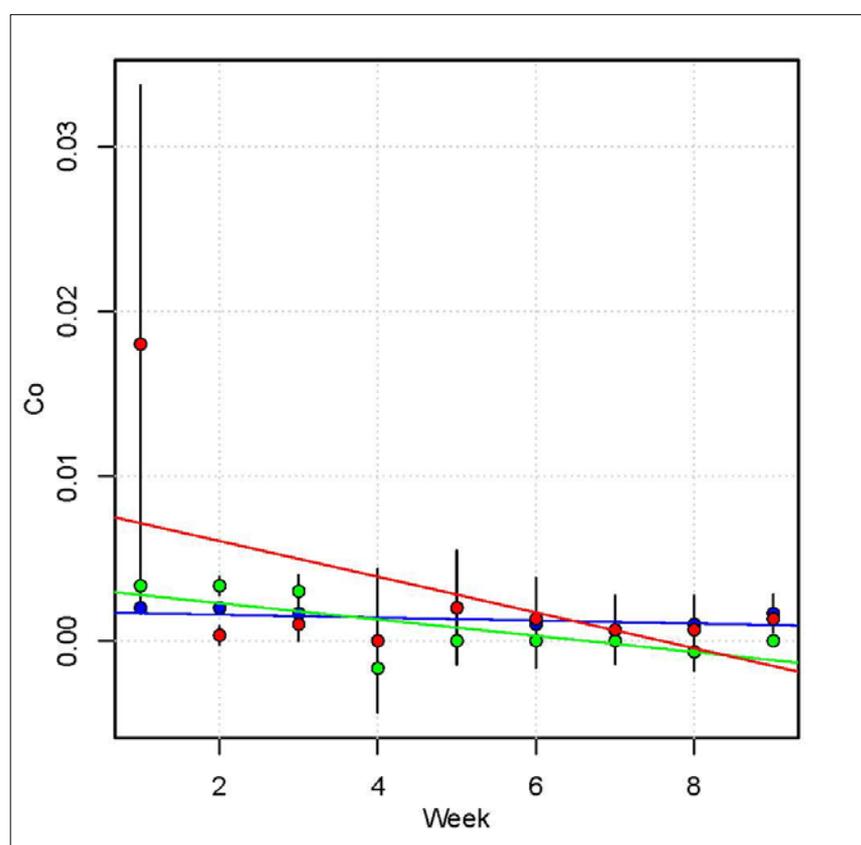


Figure 4.18 a Relationship between Fe ( mg L<sup>-1</sup>) in the discharging water from soil sorghum pots during 9 week, with irrigation frequency (1-time/week=blue color, 2-time/week=green color and 3-time/week=red color), by using linear regression function in R. The negative value on the Y-axis =treatment -control value, when value negative means that concentration of measurement higher in the control in comparison with treatment

availability and solubility; plant root exudates influence the Co bioavailability in the soil. According to Omron et al. (2012) Rajmohan et al. (2014) they discussed the Co availability in soil and their distribution among soil profile with depth, the present study showed the agreement with previous studies about metal mobility and discharging from the soil profile. In addition, in the result of subtract the value of Co that discharging from control with the value of Co that discharging from all treatments in the Fig (4.18b) showed the non-relation between Co concentration in the discharge water from soil and duration of irrigation in the (1, 2 and 3-times/week) of irrigation frequency, except the 3-time/week showed the weak-negative relation in the first week of the experiment, and also with non-significant difference in 1-time/week and 2-times/week during 9 weeks of the experiment.

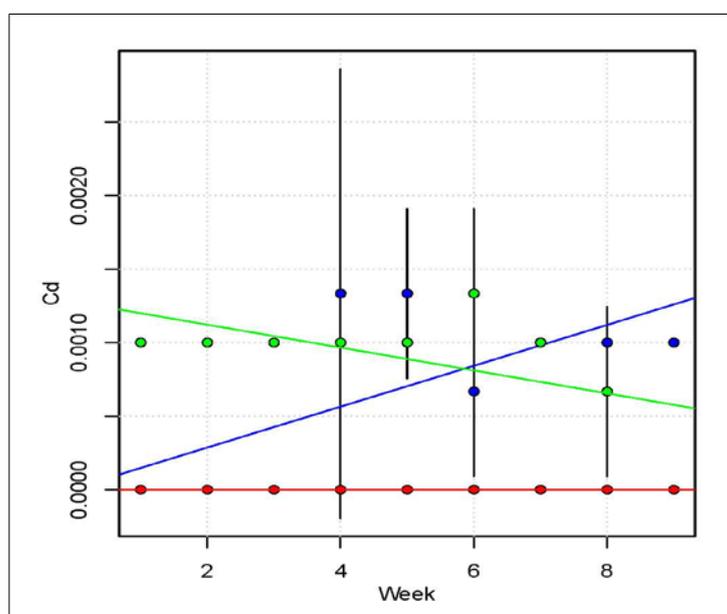


**Figure 4.18 b Relationship between Co ( mgL<sup>-1</sup>) in the discharging water from soil sorghum pots during 9 week, with irrigation frequency (1-time/week=blue color, 2-time/week=green color and 3-time/week=red color), by using linear regression function in R. The negative value on the Y-axis =treatment -control value, when value negative means that concentration of measurement higher in the control in comparison with treatment**

Cadmium has a low concentration in the irrigation water from Tanjaro River, during the experiment, the amount of Cd discharged from soil pots increased with irrigation frequency (Table 4.6), except in 3- time/week, and in the control soil pots, the results showed unexpected value (0.000 mg Cd L<sup>-1</sup>). This refers to the amount of Cd availability in the soil and

concentration of total Cd in the soil (Appendix 6 a;b). While in the (1 and 2-times /week) the excess amount of Cd discharged and available amount used by plants, and the results in the 3-time/week remain zero amount or undetectable value. Results showed agreement with Mehes-Smith et al. (2014) and Wen-ji (2016) they studied Cd distribution and discharging in the soil profile, Cd discharging from soil pot in the present study showed agreement with previous studies.

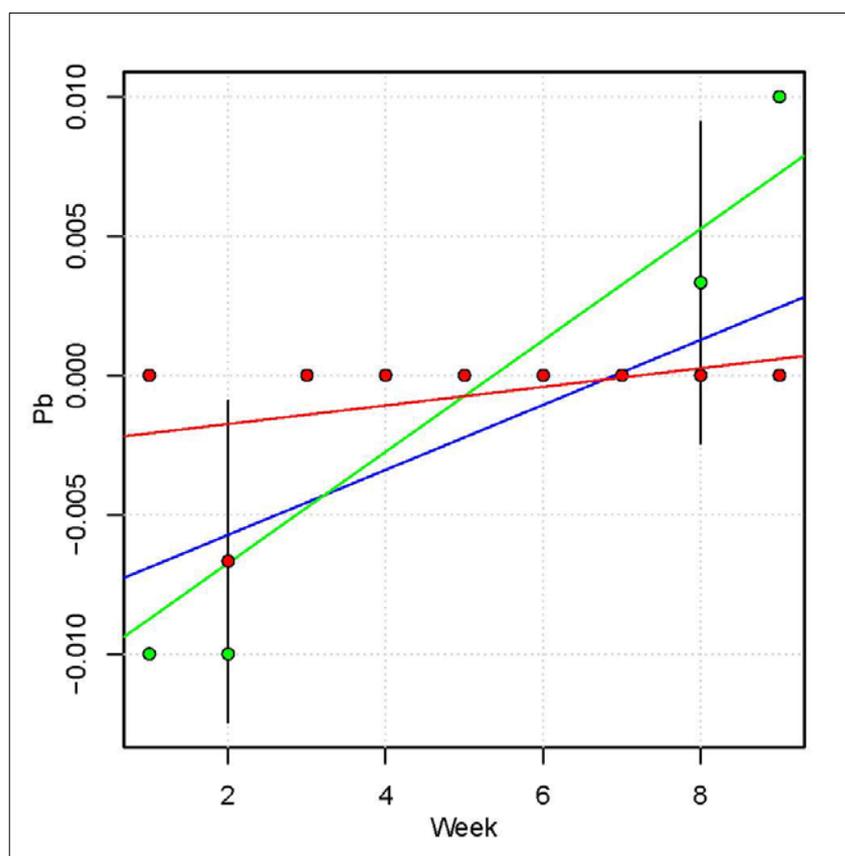
The effect of irrigation frequency on Cd discharging from the soil during the experiment showed in the Fig (4.18c), there are positive relations between Cd concentration and duration of irrigation in 1-time irrigation/week, the result showed negative relation in 2-time/week with a duration of irrigation, on the other hand in 3-time /week showed non-relation with a duration of irrigation. Moreover, there are significant differences between 1-time/week, 2-times/ week and 3-times/week of irrigation frequency against Cd concentration in the discharged water from soil pot with the period of irrigation.



**Figure 4.18 c Relationship between Cd concentration ( mgL<sup>-1</sup>) in the discharging water from soil sorghum pots during 9 week, with irrigation frequency (1-time/week=blue color, 2-time/week=green color and 3-time/week=red color), by using linear regression function in R. The negative value on the Y-axis =treatment -control value, when value negative means that concentration of measurement higher in the control in comparison with treatment**

However, the results of Pb concentration in the discharged water showed the highest value in the control, also the order of Pb concentration is Control > B > C > A in the discharge water (Table 4.6). While during the irrigation frequency, the amount of Pb discharging increased and in the 3-times/week decreased. However, there is a positive relationship between Pb concentration in the discharge water in both 1-time/week and 2-time/week of irrigation during

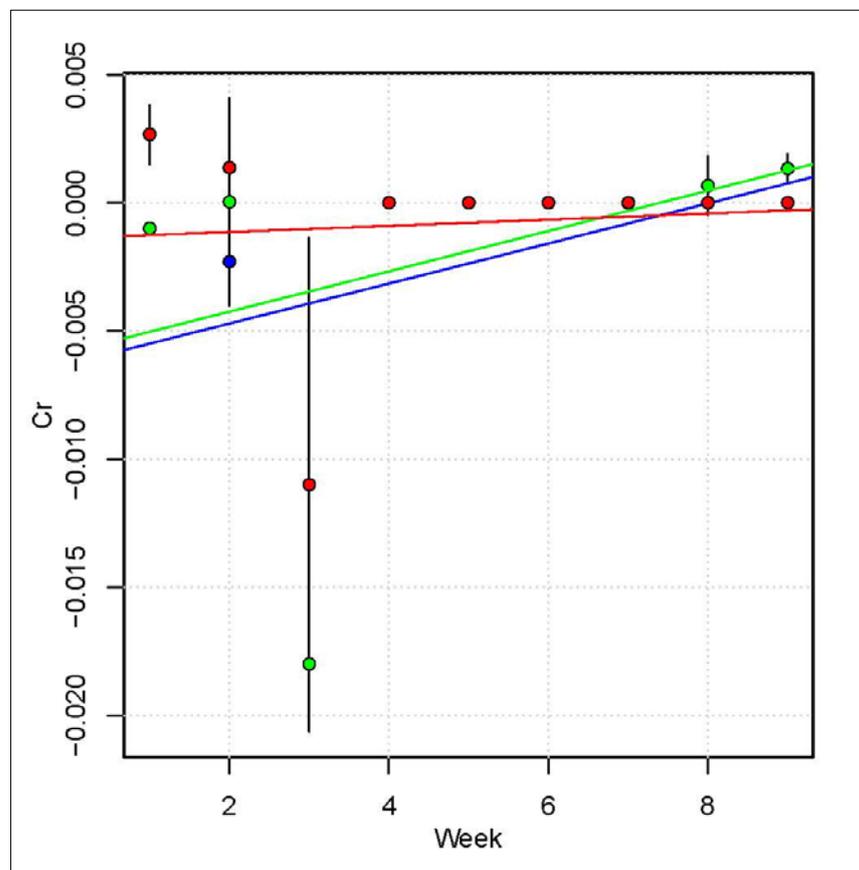
the 9 weeks (Fig 4.18d); also, the result shows non-relation between 3-time/week of irrigation. Which mean that more Pb discharging from the soil in the first time of irrigation by increasing the duration and time of irrigation more Pb leached to soil profile, there is a significant difference between the irrigation frequency during 9 weeks. In addition, Wen-ji (2016), Shaheen and Iqbal (2018) concluded that Pb discharge and increase the solubility through the soil depth.



**Figure 4.18d Relationship between Pb concentration ( $\text{mgL}^{-1}$ ) in the discharging water from soil sorghum pots during 9 week, with irrigation frequency (1-time/week=blue color, 2-time/week=green color and 3-time/week=red color), by using linear regression function in R. The negative value on the Y-axis =treatment -control value, when value negative means that concentration of measurement higher in the control in comparison with treatment**

The amount of Cr concentration in the discharging water from soil pot increased with irrigation frequency in order Control > C > B > A (Table 4.5). In addition, there are positive relations between Cr concentration in discharging water from soil during the irrigation in the 1-time/week and 2-time/week of irrigation frequency (Fig 4.18e), by increasing duration of irrigation Cr releasing increases from the soil. The results point out, the Cr released from soil because of soil contains high amount of total and soluble Cr concentration, furthermore by plant root exudate increase the Cr availability. However, there are non-relation between Cr

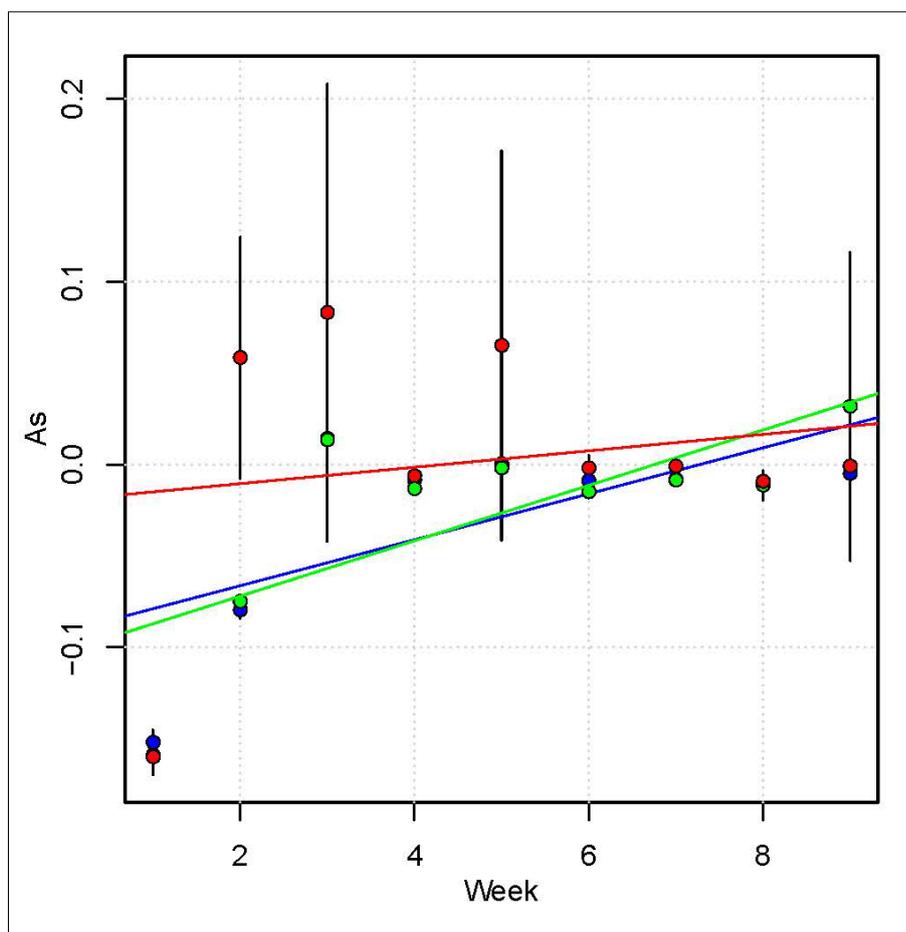
concentration in discharge water and duration of experiment for 9 weeks in 3-times/week of irrigation frequency, besides 3-times/week recorded the highest amount of Cr concentration in the discharge water. Moreover, there are significant differences between the irrigation frequency in second and third-time/week of irrigation.



**Figure 4.18e** Relationship between Cr concentration ( $\text{mgL}^{-1}$ ) in the discharging water from soil sorghum pots during 9 week, with irrigation frequency (1-time/week=blue color, 2-time/week=green color and 3-time/week=red color), by using linear regression function in R. The negative value on the Y-axis = treatment - control value, when value negative means that concentration of measurement higher in the control in comparison with treatment

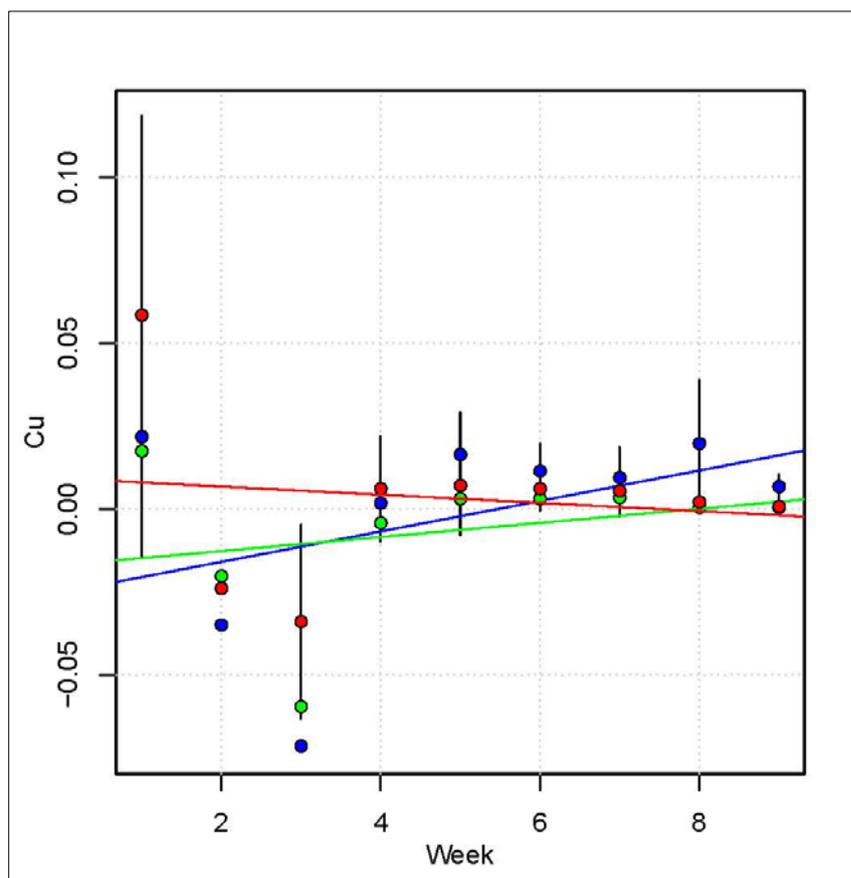
Arsenic concentration in the discharged water in the order  $C > \text{Control} > A > B$  it means that when the irrigation frequency increase the As amount increase in the discharged water, also highest value recorded in the 3-time/week (Table 4.6). The As concentration in the control lower than the treatment specifically C, this due to the plant root activity to dissolve more As in the soil. Wuana et al. (2011), discussed the As bonded to other ions as  $\text{SO}_4$  in the soil solution, which affects the As mobility. The results in Fig (4.18f) shows the positive relation between As concentration in discharge water and duration of irrigation in 1-time/week and 2-times/week of irrigation frequency and low positive relation in 3-time/week, also there is a significant difference between the irrigation frequency especially in week 2,3,5,9. While pH has a strong

effect on As, which solubility increase by increasing pH. Then the total and soluble concentration of As was high in the soil and in the irrigation water which increases in the As availability and solubility to discharge



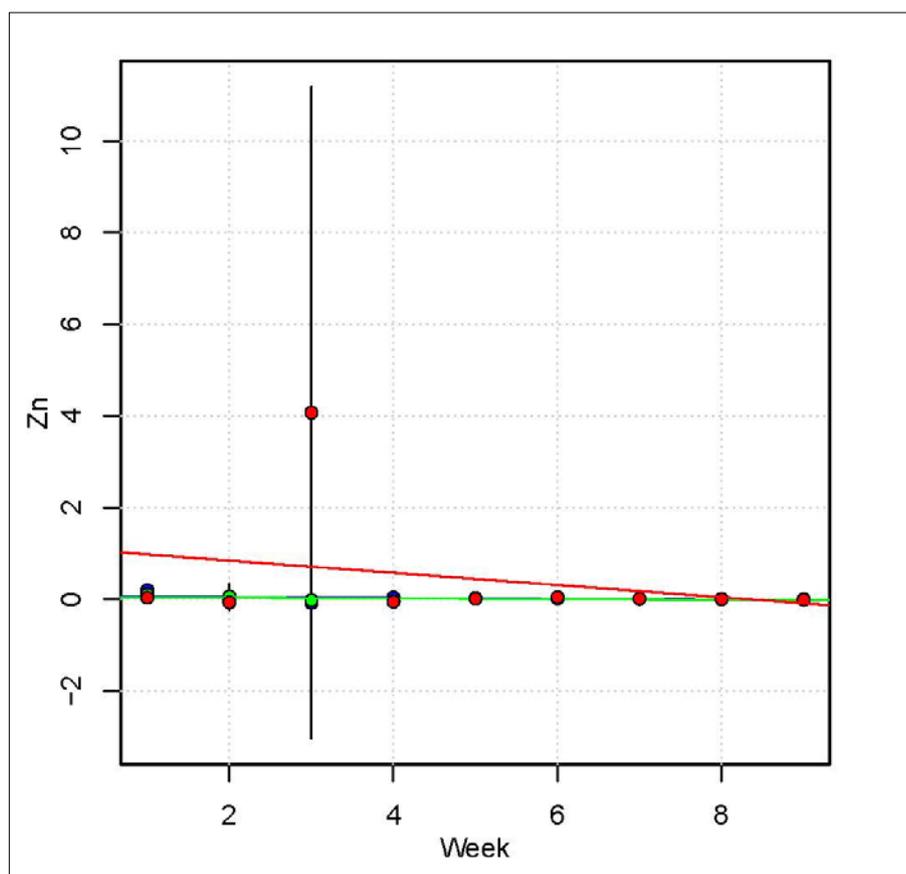
**Figure 4.18f** Relationship between As concentration ( $\text{mgL}^{-1}$ ) in the discharging water from soil sorghum pots during 9 week, with irrigation frequency (1-time/week=blue color, 2-time/week=green color and 3-time/week=red color), by using linear regression function in R. The negative value on the Y-axis = treatment - control value, when value negative means that concentration of measurement higher in the control in comparison with treatment

The results in the Fig (4.18g) showed the low positive relation between Cu concentration in the discharge water and duration of irrigation in the irrigation frequency (1-time and 2-times/weeks), also there is a low negative relation in 3-times/week, besides recorded the highest value of Cu concentration from discharge water. In addition, there is a significant difference between irrigation frequency in the first week and third week of irrigation. Also, the result investigated that; were increasing of duration with time of irrigation, increase the amount of Cu discharging from soil to underground water, Rashid, (2012) investigated the Cu leachate from soil profile.



**Figure 4.18g** Relationship between Cu concentration ( $\text{mgL}^{-1}$ ) in the discharging water from soil sorghum pots during 9 week, with irrigation frequency (1-time/week=blue color, 2-time/week=green color and 3-time/week=red color), by using linear regression function in R. The negative value on the Y-axis = treatment - control value, when value negative means that concentration of measurement higher in the control in comparison with treatment

However, the Fig (4.18h) showed weak-negative relation between Zn concentration and irrigation during 9 weeks, and there is no significant difference between the irrigation frequencies except the third week of irrigation. In addition, the 3-time/week showed the highest amount of Zn discharging from the soil.



**Figure 4.18h Relationship between Zn concentration ( $\text{mgL}^{-1}$ ) in the discharging water from soil sorghum pots during 9 week, with irrigation frequency (1-time/week=blue color, 2-time/week=green color and 3-time/week=red color), by using linear regression function in R. The negative value on the Y-axis = treatment - control value, when value negative means that concentration of measurement higher in the control in comparison with treatment**

Manganese concentration in the discharged water started from one time per week of irrigation and recorded the highest value (Table 4.6) like as Fe, except in control. In addition, the order of Mn discharging is  $A > \text{control} > C > B$ , amount of Mn in the control discharging was lower than the B and C treatment depending on Mn complexation in the soil and much commutative metal with other nutrients in the soil solution, also Rajmohan et al. (2014) established the similar results. However, there is a positive relation between Mn concentration and duration of irrigation frequency (1,2,3-times/week), and also there are non-significant difference between irrigation frequency (Fig 4.18i), the result concluded that, Mn concentration release from soil to underground water by increasing the time and duration of irrigation.

The results recognized that irrigation frequency affects on the metal discharging through the soil during the time, in addition using the long-term wastewater for irrigation affect the groundwater. The results showed agreement with Yang et al. & Rashid (2012), they concluded the distribution and leachate of heavy metals through the soil profile and Wu et al. (2017) found the concentration of the metal in the underground water during long-term of wastewater irrigation.

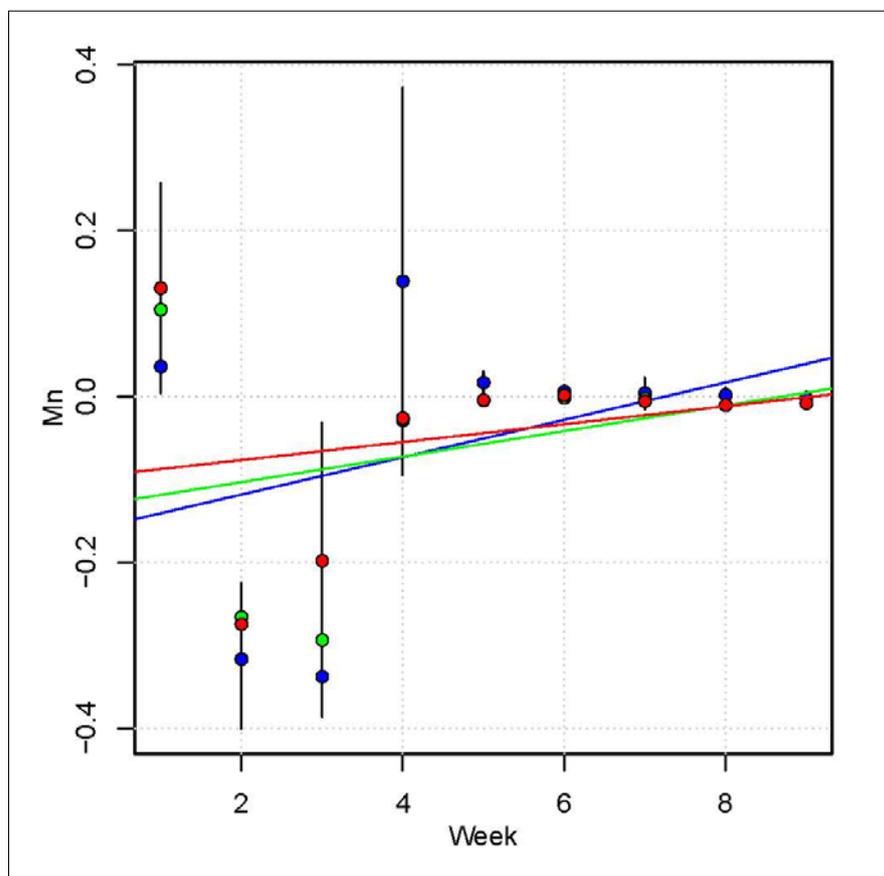


Figure 4.18i Relationship between Mn concentration ( $\text{mgL}^{-1}$ ) in the discharging water from soil sorghum pots during 9 week, with irrigation frequency (1-time/week=blue color, 2-time/week=green color and 3-time/week=red color), by using linear regression function in R. The negative value on the Y-axis = treatment - control value, when value negative means that concentration of measurement higher in the control in comparison with treatment

#### 4.2.2.2 Cations ( $\text{K}^+$ , $\text{Na}^+$ , $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$ ) concentration in the discharged water from the soil pots

The potassium value ( $8.52 \text{ mg K L}^{-1}$ ) in the irrigated water, also the results of irrigation frequency (1,2 and 3) time per week, showed decreasing in  $\text{K}^+$  concentration in the discharging water with irrigation time (Table 4.7). However, the amount of the  $\text{K}^+$  concentration discharging from control is higher than other treatment and value  $38.590 \text{ mg K}^+ \text{ L}^{-1}$ . The results showed that  $\text{K}^+$  has up taken by plant biomass during the experiment, and the concentration of  $\text{K}^+$

decreased in the discharging water. Furthermore, in the result in the Table (4.7) subtract the value of  $K^+$  that discharging from control with the value of  $K^+$  that discharging from all treatments showed a positive relationship between the  $K^+$  concentration in the discharge water and duration of irrigation (Fig 4.18j), while the results of irrigation frequency showed non-significant difference between times of irrigation per weeks. The present study investigated that by increasing of irrigation time per week doesn't have the effect of  $K^+$  discharge from soil to ground water but the duration of irrigation have a positive effect of  $K^+$  discharging through the soil, however, Oliveira et al. (2016) investigated the  $K^+$  discharge with the depth of soil.

On the other hand,  $Na^+$  concentration was discharging from soil pots increased by increasing the time of irrigation (Table 4.7), in the 3-times/ week recorded the highest value (75.88 mg  $Na^+$   $L^{-1}$ ). The discharging of  $Na^+$

**Table 4.7 Mean concentrations of cation and anions in discharge water from the soil pots during sorghum experiment**

Treatment	Irrigation Frequency	$K^+$	$Na^+$	$Ca^{2+}$	$Mg^{2+}$	$HCO_3^-$	$CO_3^{2-}$	$NO_3^{2-}$	$PO_4^{3-}$	$SO_4^{2-}$
		mgL <sup>-1</sup>								
A	1/week	9.19	72.72	336.99	31.59	131.22	6.53	7.98	2.14	9.74
B	2/week	9.11	70.95	362.96	25.39	106.88	18.30	11.55	2.44	1.53
C	3/week	8.28	75.88	308.45	22.93	95.23	28.23	5.89	3.16	0.85
Control	1,2,3/week	38.59	74.13	309.76	26.31	95.04	26.18	6.51	3.78	0.96

amount more than the  $K^+$ , this difference referred to the  $Na^+$  solubility and the  $K^+$  up taking by the plant were more than  $Na^+$ . Wakeel (2013) found the computation between  $Na^+$  and  $K^+$  efficiency and mechanisms to plant up taking from the soil solution. However, there is a negative relation between  $Na^+$  concentration in the discharge water dependent on the 2 month of irrigation, while the result in Fig (4.18k) depending on substrate  $Na^+$  control value from treatment showed the significant differences between 3-time/week and 1,2-time/week of irrigation frequency specifically in the week (1,7, 8 and 9) to  $Na^+$  discharging from soil pots during sorghum experiment.

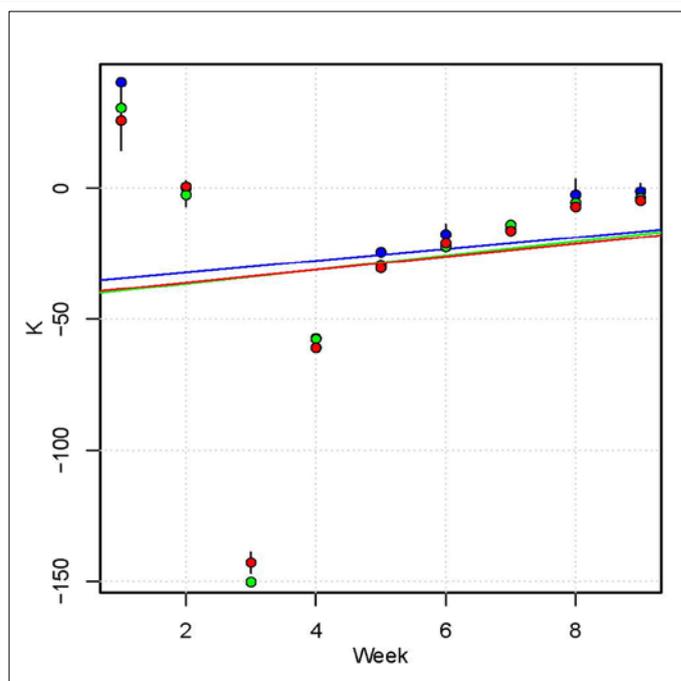


Figure 4.18j Relationship between  $K^+$  concentration ( $mgL^{-1}$ ) in the discharging water from soil sorghum pots during 9 week, with irrigation frequency (1-time/week=blue color, 2-time/week=green color and 3-time/week=red color), by using linear regression Coefficient function in R. The negative value on the Y-execs =treatment -control value, when value negative means that concentration of measurement higher in the control in comparison with treatment

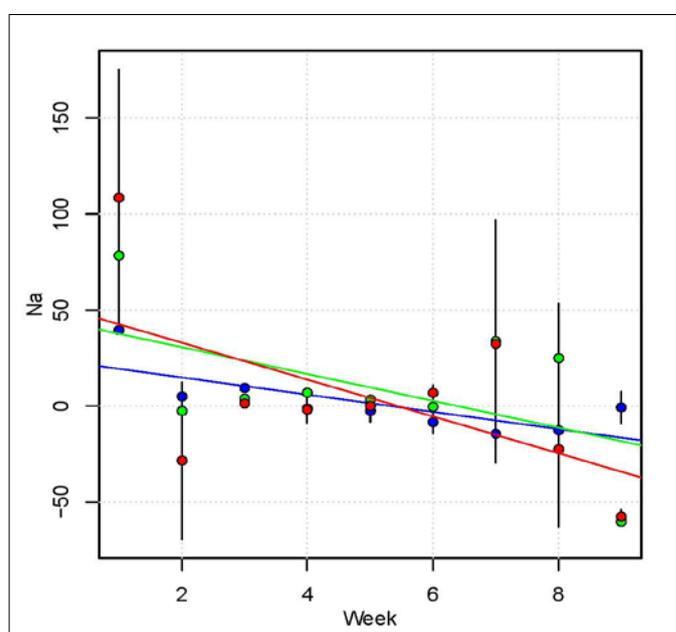


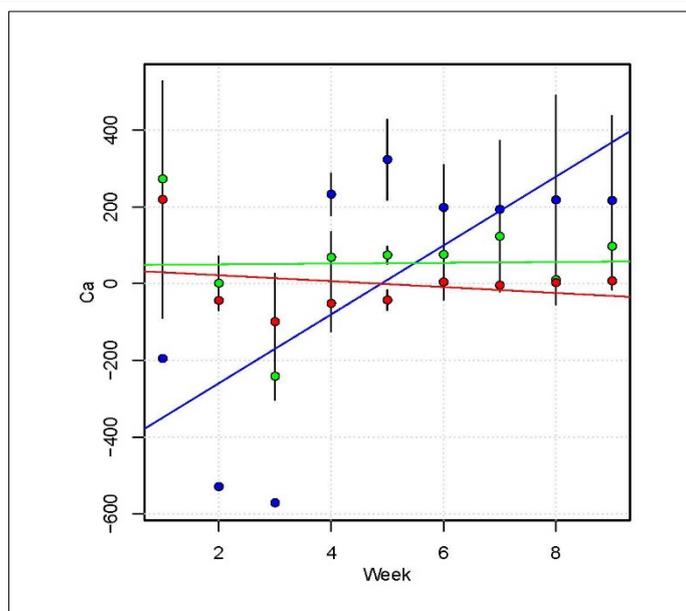
Figure 4.18k Relationship between  $Na^+$  concentration ( $mgL^{-1}$ ) in the discharging water from soil sorghum pots during 9 week, with irrigation frequency (1-time/week=blue color, 2-time/week=green color and 3-time/week=red color), by using linear regression function in R. The negative value on the Y-execs =treatment -control value, when value negative means that concentration of measurement higher in the control in comparison with treatment

In addition, the  $\text{Ca}^{2+}$  concentration in the irrigation water is  $160.38 \text{ mg L}^{-1}$  (Table 4.7), then the concentration of  $\text{Ca}^{2+}$  in the discharged water from soil pots were increased with increasing the time of irrigation per week, also the value ( $362.96 \text{ mg Ca}^{2+} \text{ L}^{-1}$ ) higher than the concentration in the irrigation wastewater. This result was acceptable depending soluble  $\text{Ca}^{2+}$  concentration in the soil (Appendix 5). In addition, there is a positive relation between  $\text{Ca}^{2+}$  concentration in the discharge water from the soil and irrigation per week in the 1-time/week of irrigation frequency, and there is non-relation in 2-time /week with low-negative relation in 3-time/week. Moreover, there are significant differences between irrigation frequencies during experiment especially between 1-time/week with both 2 and 3-time/week.

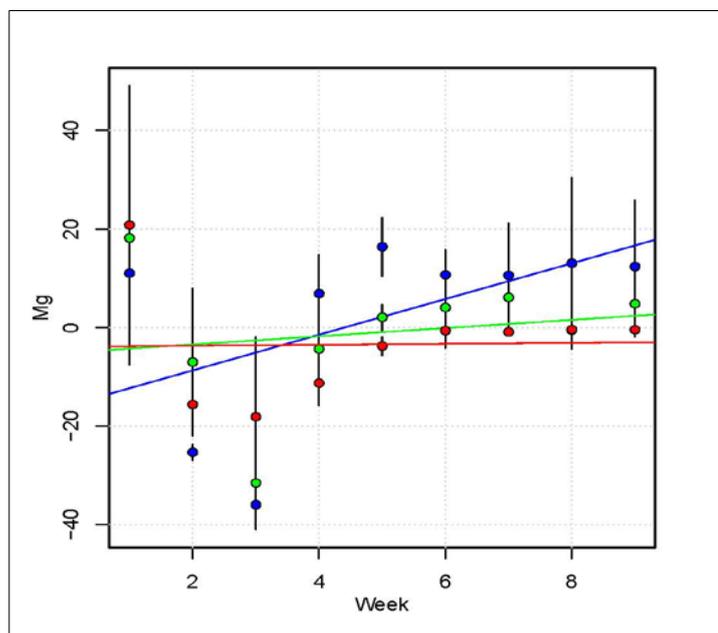
The result concluded that;  $\text{Ca}^{2+}$  concentration discharge from the soil in 1-time irrigation/week and by increasing the time of irrigation the discharge of  $\text{Ca}^{2+}$  increases from the soil during the time (Fig 4.18l).

On the other hand, the  $\text{Mg}^{2+}$  concentration in the 1-time irrigation per week was recorded highest value ( $31.59 \text{ mg Mg}^{2+} \text{ L}^{-1}$ ) in comparison with other treatments, then this value decreased with irrigation frequency (Table 4.7), this may refer to the  $\text{Mg}^{2+}$  concentration in the soil and in the irrigation wastewater. In addition, the form of  $\text{Mg}^{2+}$  is bioavailable uptake through the plant or soluble form, and in the 1-time of irrigation have discharged from the soil. However, the result of Fig (4.18m) showed a positive relationship between  $\text{Mg}^{2+}$  concentration and duration of irrigation in the 1-time/week of irrigation frequency, also there are non-relation in 2 and 3-time/week of irrigation frequency, the result investigated the significant differences between 1-time/ week and other (2 and 3-times/ week ) of irrigation frequency. The  $\text{Mg}^{2+}$  concentration released from soil by increasing the duration of irrigation.

The results of cation concentration in the discharged water showed that; the irrigation frequencies have a positive effect on the cation discharging from soil especially using the polluted water for irrigation. The results indicated that the cation can reach the ground water through the soil by repetitions of wastewater irrigation for long-term, also Rashid (2010) studied the cations leachate through the soil column in the laboratory and investigated cations solubility increase with increasing the time of water adding during the leached column experiment .



**Figure 4.18l** Relationship between  $\text{Ca}^{2+}$  concentration ( $\text{mgL}^{-1}$ ) in the discharging water from soil sorghum pots during 9 week, with irrigation frequency (1-time/week=blue color, 2-time/week=green color and 3-time/week=red color), by using linear regression function in R. The negative value on the Y-axis = treatment - control value, when value negative means that concentration of measurement higher in the control in comparison with treatment

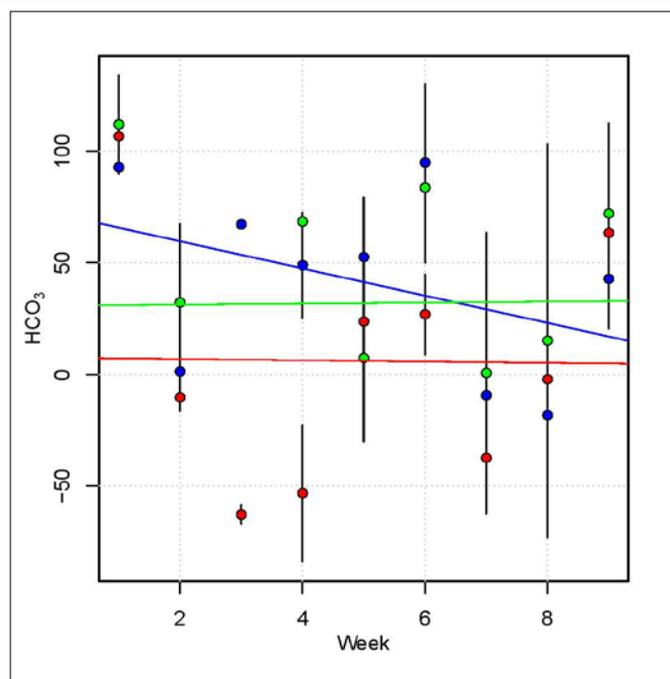


**Figure 4.18m** Relationship between  $\text{Mg}^{2+}$  concentration ( $\text{mgL}^{-1}$ ) in the discharging water from soil sorghum pots during 9 week, with irrigation frequency (1-time/week=blue color, 2-time/week=green color and 3-time/week=red color), by using linear regression function in R. The negative value on the Y-axis = treatment - control value, when value negative means that concentration of measurement higher in the control in comparison with treatment

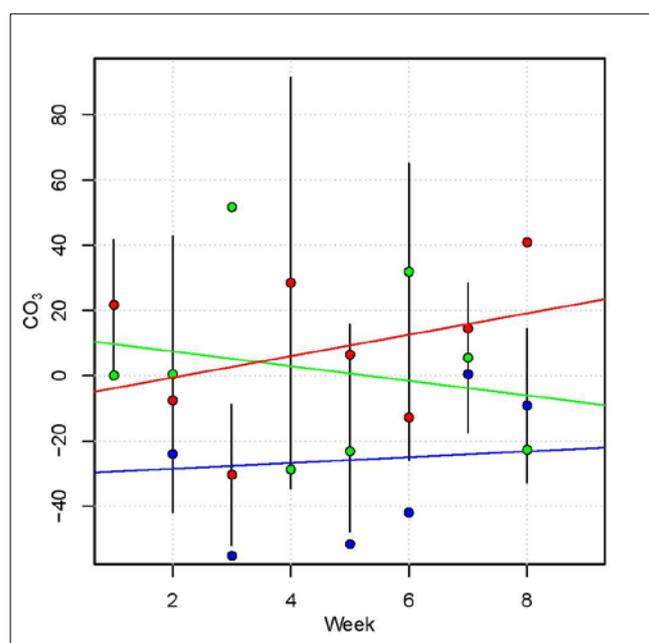
#### 4.2.2.3 Anions ( $\text{HCO}_3^-$ , $\text{CO}_3^{2-}$ , $\text{NO}_3^-$ , $\text{PO}_4^{3-}$ and $\text{SO}_4^{2-}$ ) concentration in the discharge water from the soil pots

The effect of the irrigation frequency on the  $\text{HCO}_3^-$  in the discharging water showed decreasing in  $\text{HCO}_3^-$  concentration with irrigation frequency during the experiment, the highest value ( $31.22 \text{ mg L}^{-1}$ ) was recorded in the 1-time irrigation /week (A). While the results in Fig (4.18n) showed the significant differences between the irrigation frequencies, also, there is a negative relation between  $\text{HCO}_3^-$  concentration in the discharge water from soil during the 2 month of experiment specifically in 1-time/week of irrigation; in addition, the results showed non-relation between 2 and 3-time/week of irrigation frequency. On the other hand,  $\text{CO}_3^{2-}$  showed the reverse results, where the amount of  $\text{CO}_3^{2-}$  concentration in the discharged water increased by increasing the irrigation time, and the highest value ( $28.23 \text{ mg CO}_3 \text{ L}^{-1}$ ), recorded in the 3-time irrigation /week. Moreover, the Fig (4.18o) showed a positive relationship between  $\text{CO}_3^{2-}$  concentration and irrigation time during the experiment in 3-times/week of irrigation frequency, and low positive relation in 1-time/week with non-relation in 2-time /week of irrigation frequency depending on substrate anion value of control from treatment (Table 4.7). In addition, there are significant differences between irrigation frequencies affecting  $\text{CO}_3^{2-}$  leachate from soil. Which results achieved that; by increasing the irrigation time per week more  $\text{CO}_3^{2-}$  the amount would be discharged from the soil, but  $\text{HCO}_3^-$  discharging from soil would be started through 1-time irrigation/ week, the alkalinity discharging from soil was highly connected with soil texture in the silty texture  $\text{HCO}_3^-$  discharge easily and depending on this in the 1-time irrigation maybe high amount of  $\text{HCO}_3^-$  discharged (Salimon, 1980)

The  $\text{NO}_3^-$  concentration in the discharged water from the soil pots were shown the differences level with irrigation frequency. The result recorded the highest value ( $11.55 \text{ mg NO}_3^- \text{ L}^{-1}$ ) of  $\text{NO}_3^-$  concentration in the 2-time irrigation/week. The result indicated that  $\text{NO}_3^-$  start discharging from the soil in 1-time irrigation/ week. Although the results in the Fig (4.18p) was showed the significant differences between the irrigation frequency to discharge the  $\text{NO}_3^-$  from the soil, also showed the negative relationship in (1 and 3-time irrigation/week) respectively, dependent on 9 weeks of irrigation, and the discharging of  $\text{NO}_3^-$  refer to the ion mobility through soil (Sahrawat, 2018)



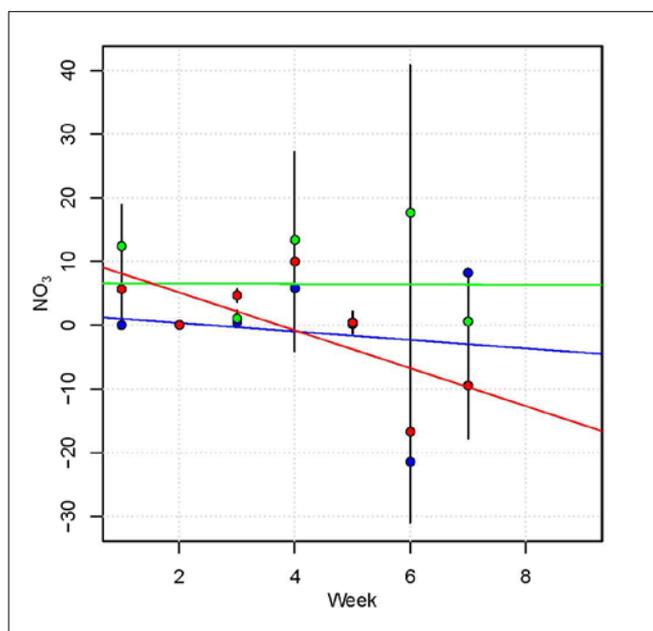
**Figure 4.18n** Relationship between  $\text{HCO}_3^-$  concentration ( $\text{mgL}^{-1}$ ) in the discharging water from soil sorghum pots during 9 week, with irrigation frequency (1-time/week=blue color, 2-time/week=green color and 3-time/week=red color), by using linear regression function in R. The negative value on the Y-axis =treatment -control value, when value negative means that concentration of measurement higher in the control in comparison with treatment



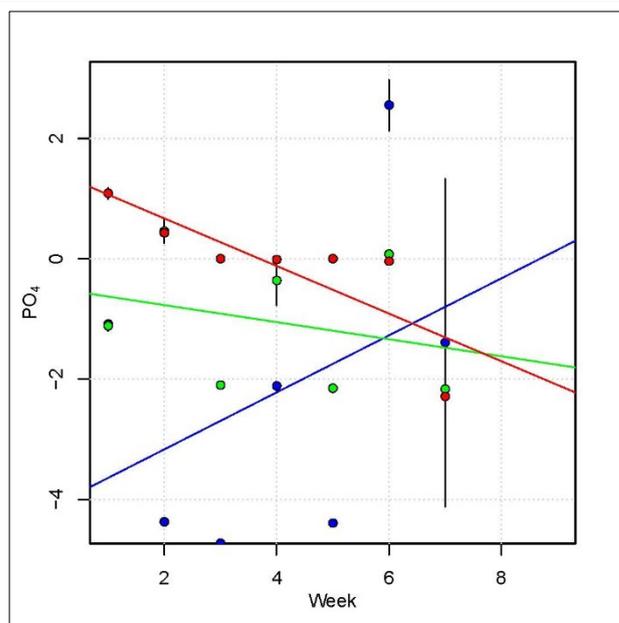
**Figure 4.18o** Relationship between  $\text{CO}_3^{2-}$  concentration ( $\text{mgL}^{-1}$ ) in the discharging water from soil sorghum pots during 9 week, with irrigation frequency (1-time/week=blue color, 2-time/week=green color and 3-time/week=red color), by using linear regression function in R. The negative value on the Y-axis =treatment -control value, when value negative means that concentration of measurement higher in the control in comparison with treatment

While  $\text{NO}_3^-$  is an essential nutrient to plant growth, with the result found the amount of  $\text{NO}_3^-$  release from the soil, especially when soil irrigated by polluted water was reached in the  $\text{NO}_3^-$ , this problem transfer to the ground water pollution.

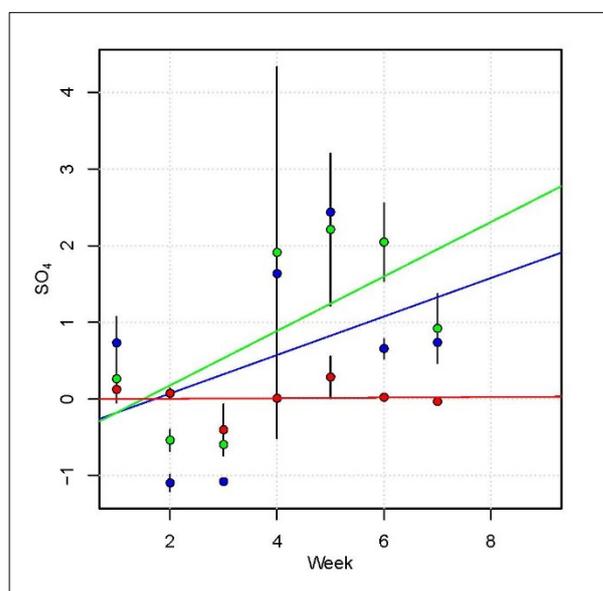
The results in Table (4.7) indicated that the  $\text{PO}_4^{3-}$  concentration decreased in the discharging water with increasing irrigation frequency. Moreover, the highest value ( $3.16 \text{ mg PO}_4^{3-} \text{ L}^{-1}$ ) recorded in the 3-time irrigation/week. While the Fig (4.18q) showed significant differences between irrigation frequency, and negative relation between  $\text{PO}_4^{3-}$  concentration in the discharge water with irrigation of 2 month of the experiment in 2 and 3-time irrigation/weeks, and have positive relationship in 1-time irrigation/week. The results have founded the  $\text{PO}_4^{3-}$  discharging from soil to groundwater, and maybe cause the environmental problem on the groundwater. On the other hand, the  $\text{SO}_4^{2-}$  discharging from the soil in the 1-time irrigation/week was recorded the highest value ( $9.74 \text{ mg SO}_4^{2-} \text{ L}^{-1}$ ) in comparison with other treatment 2-time and 3-time /week (Table 4.7). In addition, there are positive relations between  $\text{SO}_4^{2-}$  concentration in the discharge water from soil and irrigation time during the experiment in the (1 and 2-time/week) of irrigation frequency, and there are non-relation in 3-time /week (Fig 4.18r).



**Figure 4.18p** Relationship between  $\text{NO}_3^-$  concentration ( $\text{mgL}^{-1}$ ) in the discharging water from soil sorghum pots during 9 week, with irrigation frequency (1-time/week=blue color, 2-time/week=green color and 3-time/week=red color), by using linear regression function in R. The negative value on the Y-axis = treatment - control value, when value negative means that concentration of measurement higher in the control in comparison with treatment



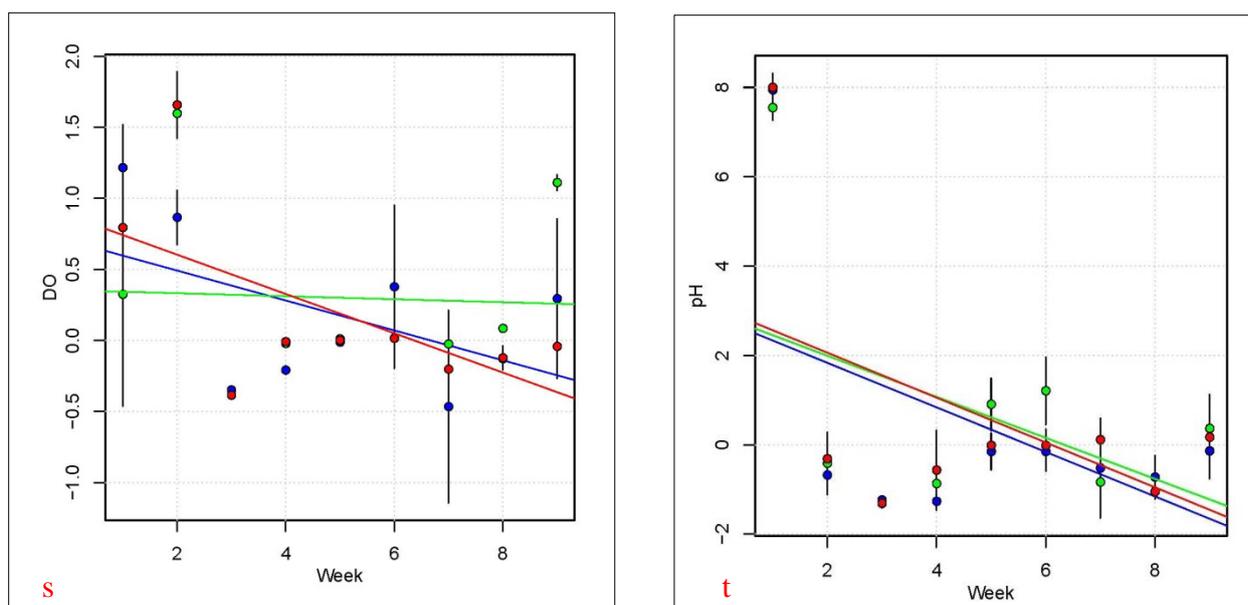
**Figure 4.18q** Relationship between  $\text{PO}_4^{3-}$  concentration ( $\text{mgL}^{-1}$ ) in the discharging water from soil sorghum pots during 9 week, with irrigation frequency (1-time/week=blue color, 2-time/week=green color and 3-time/week=red color), by using linear regression function in R. The negative value on the Y-axis = treatment - control value, when value negative means that concentration of measurement higher in the control in comparison with treatment



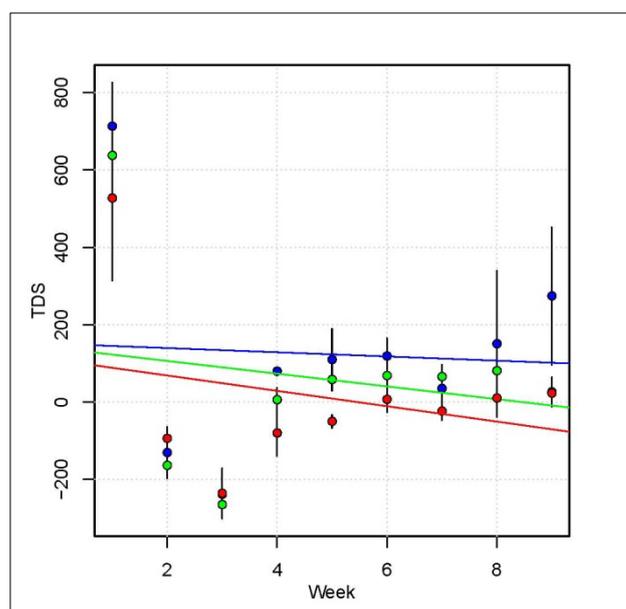
**Figure 4.18r** Relationship between  $\text{SO}_4^{2-}$  concentration ( $\text{mgL}^{-1}$ ) in the discharging water from soil sorghum pots during 9 week, with irrigation frequency (1-time/week=blue color, 2-time/week=green color and 3-time/week=red color), by using linear regression function in R. The negative value on the Y-axis = treatment - control value, when value negative means that concentration of measurement higher in the control in comparison with treatment

Generally, the results conclude that the polluted water irrigation frequency for long-term have effects on the ground water quality and soil chemistry, and Muhammed (2002); Sabbar (2018) investigate poor water quality from underground water near to Tanjaro River.

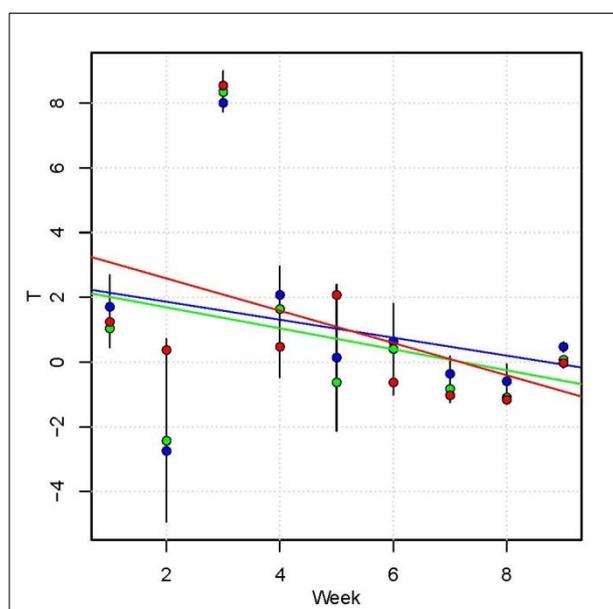
Results in Fig (4.18s,t,u,v) showed the negative relationship of (DO, pH, TDS, and T) value with irrigation time during experiment respectively, in the irrigation frequency 1, 2 and 3-time/week, except DO in 2-time/week showed non-relation. Although, there are low-significant differences between irrigation frequency. On the other hand, turbidity showed a positive relation with irrigation time during experiment under irrigation frequency 1, 2 and 3-time/week with significant differences (Fig 4.18w). Which result confirmed that by increasing of the irrigation period decreases the value of (DO, pH, Ec, TDS, and T) in the discharge water from soil except turbidity increase and this result was expected during the soil mechanisms, however, Muhammed (2002) concluded the well water pollution near to Tanjaro River .



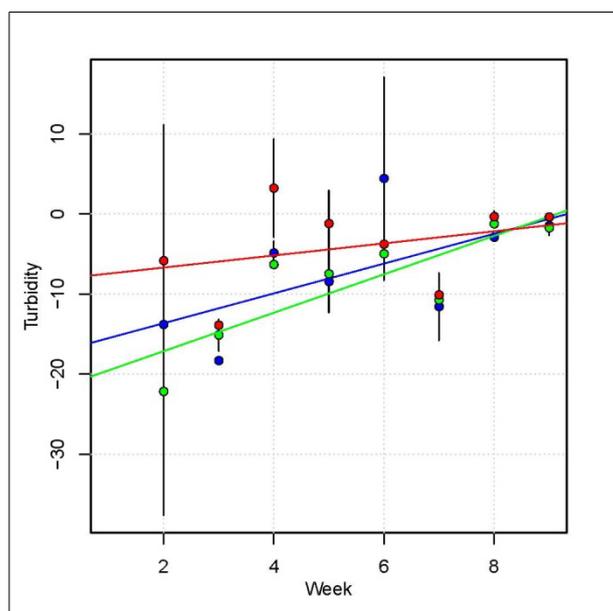
**Figure 4.18 s, t Relationship between Do  $\text{mgL}^{-1}$ , pH in the discharging water from soil sorghum pots during 9 week, with irrigation frequency (1-time/week=blue color, 2-time/week=green color and 3-time/week=red color), by using linear regression function in R. The negative value on the Y-axis = treatment - control value, when value negative means that concentration of measurement higher in the control in comparison with treatment**



**Figure 4.18 u** Relationship between TDS  $\text{mgL}^{-1}$  in the discharging water from soil sorghum pots during 9 week, with irrigation frequency (1-time/week=blue color, 2-time/week=green color and 3-time/week=red color), by using linear regression function in R. The negative value on the Y-axis =treatment -control value, when value negative means that concentration of measurement higher in the control in comparison with treatment



**Figure 4.18 v**  $T^{\circ}\text{C}$  in the discharging water from soil sorghum pots during 9 week, with irrigation frequency (1-time/week=blue color, 2-time/week=green color and 3-time/week=red color), by using linear regression function in R. The negative value on the Y-axis =treatment -control value, when value negative means that concentration of measurement higher in the control in comparison with treatment



**Figure 4.18w Relationship between Turbidity (NTU) in the discharging water from soil sorghum pots during 9 weeks, with irrigation frequency (1-time/week=blue color, 2-time/week=green color and 3-time/week=red color), by using linear regression function in R. The negative value on the Y-axis = treatment - control value, when value negative means that concentration of measurement higher in the control in comparison with treatment**

## 4.2.3 Tanjaro River irrigation frequency effects on the soil heavy metals, cations and anions

### 4.2.3.1 Heavy metals (Fe, Co, Cd, Pb, Cr, As, Cu, Zn and Mn) mg Kg<sup>-1</sup> in the soil

The Total heavy metals concentration in the soil pots during 9 weeks of sorghum experiment shows in Fig (4.19a). The effect of the irrigation frequency (1, 2 and 3-time irrigation/week) on the total heavy metals (Fe, Co, Cd, Pb, Cr, As, Cu, Zn and Mn) during 9 weeks showed the negative relation between total concentrations of (Fe and Co) in the soil pot, with the time of experiment in all irrigation frequency (1, 2 and 3- time/week). Which increasing the period of Tanjaro river water irrigation the total concentration (Fe and Co) decreased in the soil, and it is due to availability of the metals Fe and Co to discharge from pots and up taking through the plant, although there are non-significant differences between irrigation frequencies. However, the value of Fe and Co in the Table (4.8) used to obtain the Fig (4.19a) by subtract the value of Fe and Co in soil from control with the value of Fe and Co in soil from all treatments, where results in Fig (4.19a) showed the non-relation between Cd total concentrations and irrigation period. The total Cd concentration undetectable in the soil, in addition, the soluble form of Cd concentration in the soil pot showed in Table (4.8), although there are the negative relation

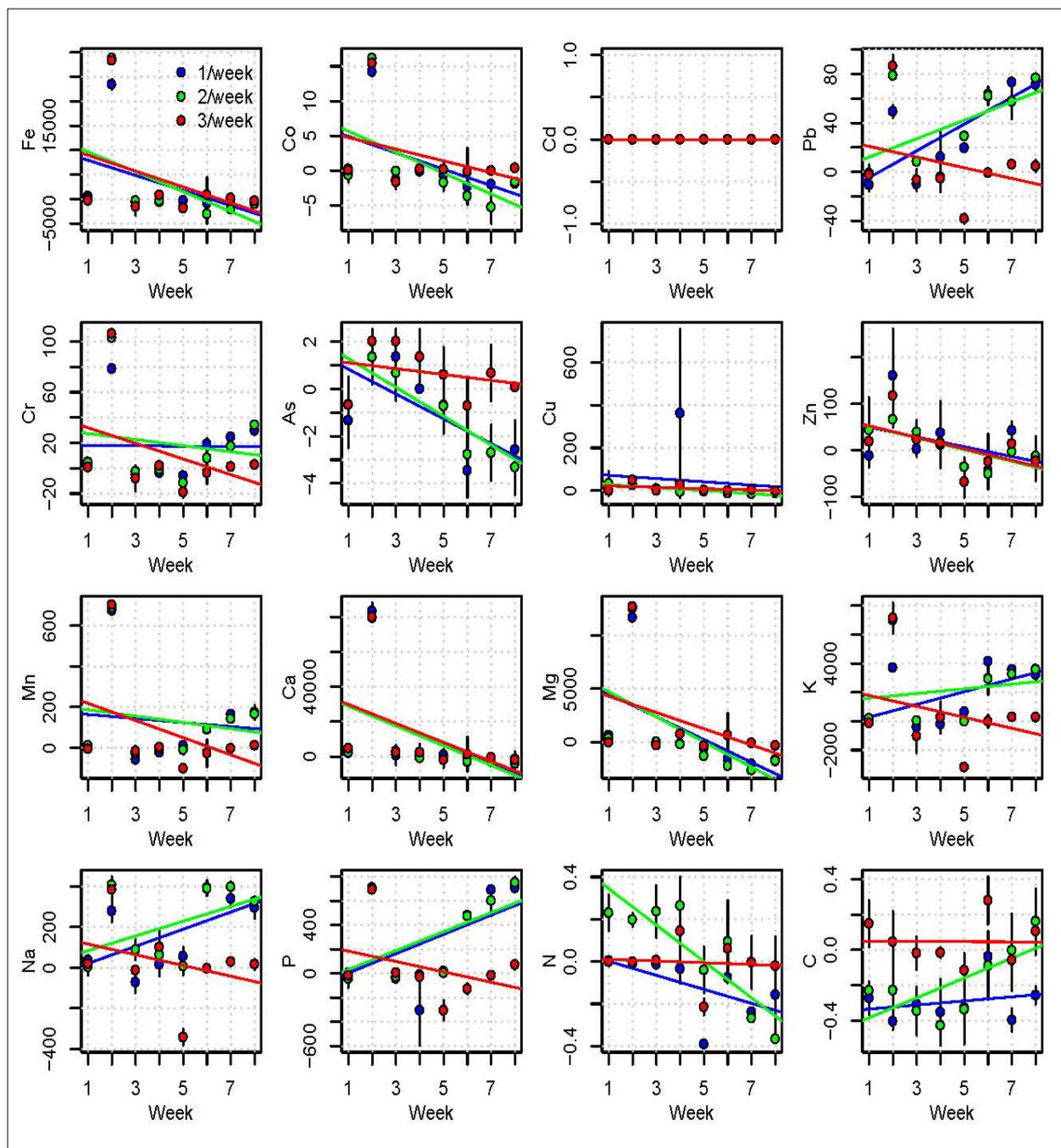
between Cd soluble concentrations and irrigation period with non-significant differences in irrigation frequency per weeks.

**Table 4.8 Mean concentration of total heavy metals mgkg<sup>-1</sup> in soil pots, during sorghum experiment (A=1time irrigation/week, B=2-time irrigation/week and C=3-time irrigation/week)**

Factor	Fe	Co	Cd	Pb	Cr	As	Cu	Zn	Mn
	mg L <sup>-1</sup>								
initial	30308.94	18.58	0.00	6.19	84.63	6.19	37.16	80.50	590.37
A	32310.63	18.11	0.00	69.81	111.93	1.80	77.34	111.37	775.12
B	28533.36	15.40	0.00	73.85	102.88	1.18	31.22	96.01	704.68
C	29270.37	16.82	0.00	40.95	94.23	2.70	38.08	97.85	643.05
Control	26004.62	15.02	0.00	35.45	83.86	2.03	27.49	88.23	572.57

Total Pb concentration in the soil increased at the end of the experiment for both (1 and 2-time irrigation/week), except the 3-time/week decreased (Table 4.8), however the result of Fig (4.19a) showed the positive relationship between Pb concentration and irrigation period in the (1 and 2-time irrigation/weeks), with non-significant differences. On the other hand, 3-time irrigation/ weeks, showed the negative relation between total Pb concentration and irrigation period. There are highly significant differences between 3-time irrigation/week and (1 and 2-time irrigation/ week), which results conclude that by increasing of irrigation frequency the Pb concentration increase in the soil at 2-time irrigation/week, above this limit effect on the Pb concentration to discharge from the soil as a form of soluble Pb. While the results in Fig (4.19a) showed higher amount of Pb concentration discharged from the soil in the 1, and 2-time irrigation/week. In addition, the results of the appendix (5) showed the higher value of soluble Pb concentration in the 3-time irrigation/ weeks.

The results of total Cr concentration in the soil pot showed the negative relation with irrigation period (Fig 4.19a), except 1-time, irrigation/ week have non-relation, and there are low significant differences between irrigation frequencies, which mean that by increasing the period of irrigation the total concentration of Cr decrease in the soil. Total concentration of As in the soil showed the negative relation with irrigation period by tanjaro River water sample under irrigation frequency (1,2 and 3-time/weeks), and the highest value (Table 4.8) of As recorded in the 3-time irrigation/week. In addition, there are significant differences between irrigation frequency and the total concentration of As decreased from the soil during the experiment.



**Figure 4.19a** Relationship between total concentration of (Fe, Co, Cd, Pb, Cr, As, Cu, Zn, Mn, Ca, Mg, K, Na, and P mg Kg<sup>-1</sup>) & (%N and %C) in the soil with irrigation for 9 weeks, under irrigation frequency (1-time/week=blue color, 2-time/week=green color and 3-time/week=red color), by using linear regression function in R, The negative value on the Y-axis =treatment -control value, when value negative means that concentration of measurement higher in the control in comparison with treatment

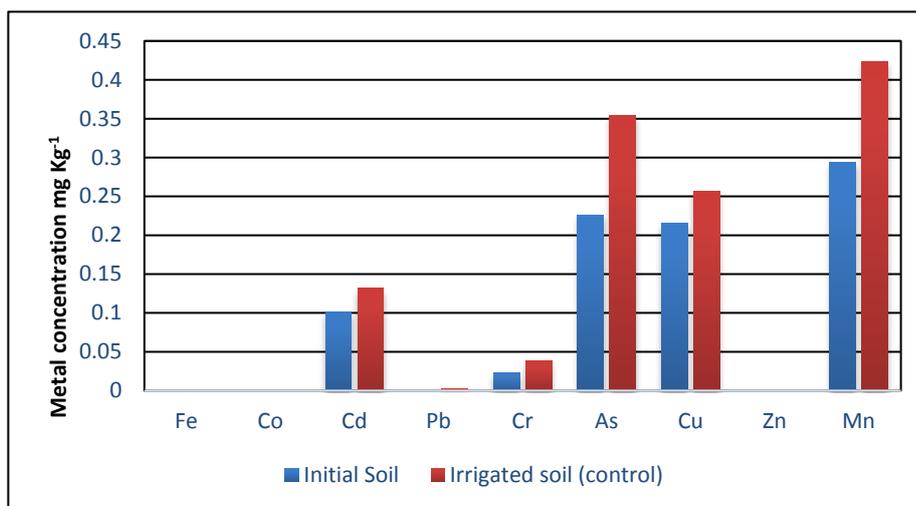
The results of (Cu, Zn and Mn) total concentrations in the soil showed the negative relation with irrigation period for 9 week by wastewater (Fig 4.19a), and with low-significant differences between irrigation frequency, which the heist value (77.34, 111.37 and 775.12 mg k<sup>-1</sup>) of (Cu, Zn and Mn), respectively recorded in the 1-time/week (Table 4.8).

Generally, the results of total and soluble heavy metals showed the similar trend, which the concentration decreases with increasing the period of irrigation during the experiment, this due to increasing of solubility to discharge from soil to underground, and also through increasing of bioavailability to plant up taking. The present study investigated that irrigating the soil for long-term had been the effect on the metal solubility and availability. Muhammed (2002); Wu et al. (2017); Chaoua et al. (2018) investigated the metals increasing in the soil after irrigation by wastewater for long-term and this agrees with our finding of increasing metals concentration in the control where irrigated with wastewater.

Increases percentage of soluble metals in the control soil in comparison to initial soil during sorghum experiment shows metals increasing in order (Mn > As > Cu > Cd > Cr > Pb) except (Fe, Co and Zn) (4.19b). Soluble metals concentration increased in the control soil pots after irrigated by Tanjaro River water and percentage of increasing are 70.48%, 56.85, 43.96%, 27%, and 19.12% for Cr, As, Mn, Cd, and Cu respectively (Appendix 6), may be metals backgrounds in the soil did not have an effects on metals increasing in the control soil, where the results in the appendix (6a) clarify high amount of total metals concentration in the initial soil in order Fe > Mn > Cr > Zn > Cu > Co > As = Pb. However, the increasing of soluble metals in control soil refer to the metals from Tanjaro River water and their mobility in the soil, increasing of specific metals solubility and availability in the soil solution, research need more study about bioavailability of those heavy metals. Results concluded that; when the soil irrigated by the water from Tanjaro River the metals had been accumulated in the soil as soluble form.

#### **4.2.3.2 Cations (Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup> and K<sup>+</sup>) concentrations mg Kg<sup>-1</sup> in the soil pots**

Essential cation Ca<sup>2+</sup> and Mg<sup>2+</sup> total concentrations in Table (4.9) used to obtain the Fig (4.19a) by subtract the value of Ca<sup>2+</sup> and Mg<sup>2+</sup> in soil from control with the value of Ca<sup>2+</sup> and Mg<sup>2+</sup> in soil from all treatments showed in the Fig (4.19a). Which results shows the negative relation between Ca<sup>2+</sup> and Mg<sup>2+</sup> concentration with irrigation period and there are non-significant differences between irrigation frequency/weeks, except week 6 have low-significant differences. The results investigated that the irrigation frequency does not influence the Ca<sup>2+</sup> and Mg<sup>2+</sup> concentration, nonetheless the Ca<sup>2+</sup> and Mg<sup>2+</sup> decreased by the period of irrigation, the same trend is exact for long-term irrigation field.



**Figure 4.19b** Metals concentration in the control soil with initial soil before irrigation during 9 week of sorghum experiment

However, the total  $K^+$  and  $Na^+$  in the soil pots showed a positive relation with the period of irrigation, except 3-time irrigation/week have negative relation, and there is a significant difference between irrigation frequencies. This results is expected, because of polluted water high in salinity, by the period of irrigation the discharge increases of salt and the concentration of  $K^+$  and  $Na^+$  decreased in the soil, also the results of Table (4.9)) showed the decreasing of Soluble  $K^+$  and  $Na^+$  in the soil with the period of irrigation, with non-significant differences between irrigation frequency. On the other hand, in Fig (4.19a) the  $K^+$  concentration increases in the discharge water by the period of irrigation. In addition, plant used ( $K^+$  and  $Na^+$ ) as an essential nutrient for growth especially potassium. However, Carlos et al. (2016) concluded the cations increasing in the soil through irrigation of wastewater.

**Table 4.9** Mean concentration of cation and anion mgkg<sup>-1</sup> in soil pots, during sorghum experiment (A=1time irrigation/week, B=2-time irrigation/week and C=3-time irrigation/week)

Factor	Ca <sup>2+</sup>	Mg <sup>2+</sup>	K <sup>+</sup>	Na <sup>+</sup>	P	%N	%C
initial	82112.61	14530.05	4130.51	103.21	171.33	0.55	4.44
A	90893.38	14706.62	6723.40	398.91	698.54	0.25	4.42
B	79344.65	12719.70	6545.67	428.29	700.23	0.34	3.97
C	81131.60	13750.12	4841.25	241.80	428.52	0.29	4.21
Control	70290.34	12117.12	4382.16	217.46	394.71	0.30	4.16

#### 4.2.3.3 Total Phosphate (P) concentration mg Kg<sup>-1</sup> in the soil

The total P concentration in the soil showed a positive relation with irrigation period by polluted water with non-significant differences in both 1 and 2-time irrigation/week (Fig 4.19a). On the other hand, there is negative relation between total P concentration and irrigation period under 3-time irrigation/week. The results concluded that which irrigated soil 2-time per week with wastewater, the amount of total P increase in the soil and when the frequency of irrigation increased to 3-time/week, total P concentration decreases in the soil, due to increasing of solubility and up taking by the plant. In addition, the results in the Table (4.9) showed the negative relation between the irrigation period and the soluble concentration of P, it means that by increasing the irrigation period the soluble form decrease from the soil, while part of the soluble form was used through plants. Yang et al. (2012), investigated the increasing of soil chemistry during wastewater irrigation for long-time on the farm land, and increasing on the P ion in the soil.

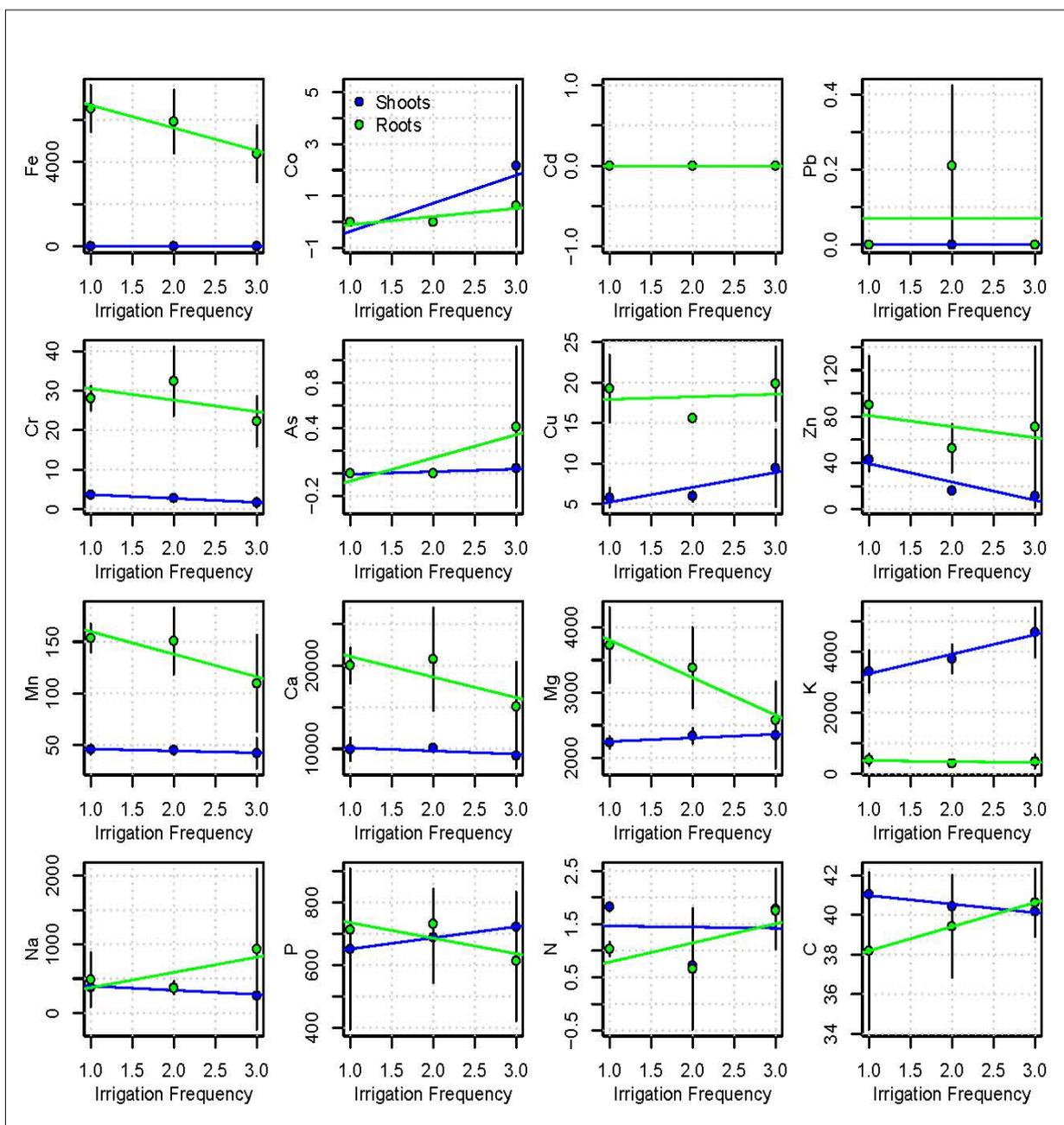
#### 4.2.3.4 Total Nitrogen (N) and Carbon (C) percentage in the soil pots

The total percentage of N in the soil shows in Fig (4.19a), and there is a negative relation between %N and irrigation period under irrigation frequency (1, 2 and 3-time/week), with significant differences between irrigation frequency. The results investigated that by increasing of irrigation period the amount of total N decrease in the soil, this refers to increase of available and soluble form of N in the soil, and my uptake by plant or discharged from soil to underground, and also the irrigation frequency have the effect of total N decreasing in the soil (Yang *et al.*, 2012),. However, the highest value (% 0.341) of %N recorded in the 2-time irrigation/week Table (4.9) Nitrogen is one of the most essential nutrients to plant and effect on the plant biomass. Moreover, the results supported by N concentration in the sorghum biomass were the highest value in the (1 and 3-time irrigation/week during the experiment (Fig 4.19a). The results of total % C in the soil during the sorghum experiment shows in the Fig (4.19a), and there is a positive relationship between % C and irrigation period under (1 and 2-time irrigation/week), on the other hand, showed the non-relation in 3-time irrigation/week during experiment. In addition, there are highly significant differences between irrigation frequency and % C in the soil pot. The results explained that; total % C increased in the soil were irrigated by wastewater for longest of the period (Xu *et al.*, 2010 Yang *et al.*, (2012). The irrigation by Tanjaro River have an effect on the carbon amount in the plant, which the amount of total %C increased in the sorghum plant gradually by irrigation frequency during the experiment (Fig 4.19)

#### **4.2.4 Irrigation frequency of Tanjaro River water affecting on the metals and nutrient concentration in the sorghum plant**

##### **4.2.4.1 Heavy metals concentration (Fe, Cr, Cu, Cd, Pb, Co, As, Zn and Mn) mgKg<sup>-1</sup> in the sorghum roots and shoots**

The results of metals concentration in the plant shoot and root showed in the Fig (4.20), generally the concentration of metals higher in the sorghum root in comparison with plant shoot, except Co concentrations. Although there are negative relations between (Fe, Cr, Zn and Mn) concentrations in plant root with irrigation frequency, where there are significant differences between metals (Fe, Cr, Zn and Mn) concentrations in the root with irrigation frequency (Appendix 7a). The results showed that the irrigation frequency /week have an effect on the metal concentration in the plant root, also by increasing of irrigation time per week the concentration of metals (Fe, Cr, Zn and Mn) were decreased in the root. However, the results of (As and Cu) concentration in the sorghum root showed a positive relationship with irrigation frequency, and there are significant differences between irrigation frequency with (As and Cu) concentration in the root (Appendix 7a). Results found that; were increasing of irrigation time per week increases the (As and Cu) concentration in the sorghum root. The results in Fig (4.20) showed the non-relation between (Cd and Pb) concentration in the sorghum root with irrigation frequency, and showed a non-significant difference between Cd with irrigation frequency, while there is significant difference between Pb with irrigation frequency. However, results showed that under 1-time irrigation/ week higher value of metals (Fe, Zn and Mn) concentration recorded, Pb and Cr concentration showed higher value under 2-time/week. (Zhuang *et al.*, 2009).



**Figure 4.20** relationship between metals and nutrient concentrations ( $\text{mg Kg}^{-1}$ ) with percentage of (N and C) in the sorghum shoot and root in the end of experiment during 60 days, the blue line=shoot and green=root, by using linear regression function in R

#### 4.2.4.2 Cations ( $\text{Ca}^{2+}$ , $\text{Mn}^{2+}$ , $\text{Na}^+$ , $\text{K}^+$ ) concentrations $\text{mg Kg}^{-1}$ in the sorghum roots and shoots

The results in Fig (4.20) showed the  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations in the sorghum, and the concentration was higher in the roots in comparison with plant shoots. Then there are negative relations between  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  Concentration in the root with irrigation frequency. In addition, results in Appendix (7a) showed significant differences between irrigation frequency

in ( $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) concentration in the plant root there are a higher concentration of ( $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) in the root under 1 and 2-time irrigation/week, respectively. On the other hand, the concentration of ( $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) in the shoot showed low (negative and positive) relation respectively, with irrigation frequency (Fig 4.20). In addition, there are significant differences between irrigation frequency/week and ( $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) concentration in the shoot were higher  $\text{Ca}^{2+}$  concentration recorded under 2-time irrigation/week, while a higher concentration of Mg recorded under 3-time irrigation/week (Appendix 7b). Results conclude that,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentration in the sorghum plant shoot and roots affected by irrigation frequency during the experiment, Feng et al. (2018) they studied the accumulation of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  by sorghum plant and shows the ability of sorghum to uptake the  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  from the soil solution.

However the result of  $\text{K}^+$  concentration showed higher concentrations in the sorghum shoot and there has a positive relationship with irrigation frequency (Fig 4.20), while the irrigation frequency showed the significant differences with  $\text{K}^+$  concentration in the shoot (Appendix 7b), then the higher concentration in the shoot recorded under 3-time irrigation/week. On the other hand,  $\text{K}^+$  concentration in the root showed non-relation with irrigation frequency; also, there are low significant differences between the irrigation frequency and  $\text{K}^+$  concentration in the root (Appendix 7a), the higher concentrations of  $\text{K}^+$  in the roots were recorded under 1-time irrigation/week.

The results in Fig (4.20) showed a positive relation between  $\text{Na}^+$  concentration in the sorghum root with irrigation frequency, and higher concentration in comparison with shoots. In addition, there are significant differences between irrigation frequency and  $\text{Na}^+$  concentration in the sorghum root were higher concentration recorded under 3-time irrigation/weeks (Appendix 7a). Sorghum shoot concentration of  $\text{Na}^+$  showed negative relation with irrigation frequency (Fig 4.20), although there are significant differences between irrigation times per week, and a higher concentration of  $\text{Na}^+$  in the shoot recorded under 1-time irrigation/weeks (Appendix7b). Present studies conclude that,  $\text{Na}^+$  and  $\text{K}^+$  concentration in the sorghum shoot and roots have affected under irrigation frequency during the experiment.

#### **4.2.4.3 Total phosphate (p) concentrations $\text{mg Kg}^{-1}$ and total (%N and %C) in the plant roots and shoots**

The results in Fig (4.20) showed the cross line of P concentration in the sorghum were there have negative relation in the root and positive relation in the shoot with irrigation frequency, while the cross point was under 2-time irrigation/week. In addition, there are significant differences between irrigation frequency with P concentration in the root and shoots.

Percentage of total N in the sorghum shoot and root shown in Fig (4.20), results showed non-relation between %N with irrigation frequency in the shoot, then there are positive relationship in % N in the root with irrigation frequency during the experiment. While there are significant differences between irrigation frequency and % N in the roots and shoots (Appendix 7 a; b). Moreover, the C percentage in the sorghum shoot higher than root and there is a negative relation between the percentage of C in the shoot with irrigation frequency (Fig 4.20), also there are significant differences between irrigation time/week during experiment. In addition, the percentage of C in the sorghum root showed a positive relation with irrigation frequency and recorded the significant differences between irrigation times per weeks (Appendix 7a).

The results investigated that were sorghum planted under irrigation frequency, have the ability to uptake the anion from the soil solution and the concentration of anions in the root and shoot significantly affected by irrigation time/week during experiment. Serafin et al. (2018) found that the most important nutrient controlling sorghum growth rate is N, P with K and Pinto et al. (2004) studied that the amount of C and N in the sorghum plant have effects on the micronutrients uptake.

### **4.3 The Biological Accumulation Coefficient (Factor) (BAC) in Sorghum**

The ability of sorghum to uptake heavy metals from soil expressed as a ratio of metals concentration in the plant to metals concentration in soil. When the value of biological accumulation of (BAC, BCF, BEF and TF) are more than (1), it is means that plant could accumulation of metals from soil and accumulate it in the specific part of plant depending on factor (Yoon et al, 2006; Li et al., 2019).

Results in Table (4.10) shows that sorghum have ability to accumulate metals Cr in there biomass depending on  $BAC > 1$  and the maximum value (41.61) respectively, recorded in the 2-time irrigation/week (B), while can accumulate Fe, Zn and As and maximum value in the 1-time irrigation / week, accumulation of Co and As recorded only in the 3-time irrigation/ week and 1 and 2-time irrigation/ week values of  $BAC < 1$ , where sorghum can not accumulate the Cd concentration in there biomass and BAC of Cd is  $< 1$  in all irrigation frequency. The biological concentration factor (BCF) represent the concentration of metals in plant root to metals in the soil, when value is  $> 1$  plant can phytostablizing the heavy metals through there root system. Sorghum shows that have ability to biostablize metals (Fe, Zn and Mn) in there root system and maximum value recorded when irrigated one-time per week, Cadmium cant not stabilize and accumulate by sorghum root as shown in Table (4.8) and value of  $BCF < 1$ , where accumulate the metals (Co, Cu and As) in the root and maximum vale in the 3-time irrigation/ week, but both Co and As dos not shown an effects by 1 and 2-time irrigation / week

and value of BCF  $<1$ , the results of BCF of Cr is  $>1$  and maximum value in 2- time irrigation/ week, sorghum can accumulate the pb in there root only when irrigated 2-time/ week as shown in the Table (4.10). The ability of sorghum to phytoextraction of metals shown in the Table (4.10), and expressed by shoot concentration of metal/ metals concentration in the soil if (BEF)  $>1$  it means sorghum have ability to extraction of metals through the shoot system. The BEF of metals Fe, Cd and Pb is  $<1$ , except Co in the 3-time irrigation/ week, sorghum BEF  $>1$  for metals (Cr, Cu, Zn and Mn), and maximum value recorded in the 1-time irrigation/week, except Cu in the 3-time irrigation/week, on the other hand sorghum cannot extract the metals Fe, Cd, Co and Pb by shoot system, except Co under 3-time irrigation/ week.

**Table 4.10 Biological Accumulation Coefficient (BAC), Biological Concentration Factor (BCF), Biological Extraction Factor (BEF) and Translocation Factor (TF) of sorghum heavy metals**

Accumulation Factor of Metals	Irrigation Frequency	Fe	Co	Cd	Pb	Cr	As	Cu	Zn	Mn
BAC	A 1-time/week	21.56	0.00	0.00	0.00	37.46	0.00	67.33	165.45	33.72
	B 1-time/week	19.53	0.00	0.00	3.39	41.61	0.00	58.04	85.38	33.17
	C 1-time/week	14.48	15.04	0.00	0.00	28.28	7.35	78.89	102.56	25.68
BCF	A 1-time/week	21.56	0.00	0.00	0.00	33.17	0.00	51.79	111.97	25.99
	B 1-time/week	19.53	0.00	0.00	3.39	38.30	0.00	41.98	65.49	25.54
	C 1-time/week	14.48	3.39	0.00	0.00	26.30	6.63	53.49	88.29	18.57
BEF	A 1-time/week	0.00	0.00	0.00	0.00	4.29	0.00	15.54	53.48	7.73
	B 1-time/week	0.00	0.00	0.00	0.00	3.32	0.00	16.06	19.89	7.63
	C 1-time/week	0.00	11.65	0.00	0.00	1.97	0.72	25.40	14.27	7.11
TF	A 1-time/week	0.00	0.00	0.00	0.00	12.94	0.00	30.00	47.76	29.75
	B 1-time/week	0.00	0.00	0.00	0.00	8.66	0.00	38.25	30.37	29.87
	C 1-time/week	0.00	343.31	0.00	0.00	7.51	10.88	47.48	16.17	38.30

The decision about which part of sorghum more active to accumulate the metals the TF , express the metals concentration in the shoot / root in the plant, if value  $>1$  it means that sorghum have ability to extraction and transfer the metals to shoot system. And the value of TF for metals (Cr, Cu, Zn and Mn) are  $>1$ , the maximum value recorded in 1-time irrigation/ week for both (Cr and Zn), maximum value of TF recorded in the 2 and 3-time irrigation/ week for Cu and Mn

respectively. Sorghum cannot transfer metals ( Fe, Co, Cd and Pb) to their shoot system, except Co under 3-time irrigation/week.

The results in the present study concluded that; Tanjaro River should be direct use as an irrigation source for type of the plants include the biotechnology of biofuel or biofertilizer as investigated by Goleman et al. (2019) & Głab and Sowinski (2019) like as sorghum, potentially using Tanjaro River water as a source of irrigation can harm the soil and plant. It would need yearly research and monitoring.

## CHAPTER FIVE

### CONCLUSION AND RECOMMENDATION

#### 5.1 Original Contribution

Depending on the international and local research, our research study originally studied the points below:

1. Algae and duckweed were, for the first time, cultivated (without amendment of nutrients to the water) and tested for remediation capacity of metals and physiochemical characteristic in the Tanjaro River in Kurdistan-Iraq.
2. Water polluted from the Tanjaro River was used to examine irrigation frequency effects on the physiochemical characteristic of soil and discharged water from the soil.
3. This is first-time sorghum plants were used to decrease the effects of polluted Tanjaro River water for irrigation soil in Kurdistan-Iraq.

#### 5.2 Conclusions

The present study concluded that:

1. Physiochemical properties of Tanjaro River water showed the Tanjaro River to have good conditions for use as a media for both algae and duckweed cultivation due to it being rich in nutrients for growth.
2. The efficiency of algae and duckweed to remove excess nutrients in the polluted water from the Tanjaro River is different. Although algae had a high efficiency to remove nutrients ( $\text{NO}_3^-$ , Co, Cu, Zn, Mn) in comparison with duckweed, duckweed had efficiency to remove the nutrients,  $\text{PO}_4^{3-}$ ,  $\text{Cl}^-$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ , in the polluted water. In general, both algae and duckweed have equality ability to remove 100 % of Fe, Cd, Pb, Cr, As,  $\text{K}^+$ .
3. The microphytes and macrophytes have the capacity to improve the Tanjaro River water for irrigation, microphytes (algae) capability to improve 8% from 50 L water, and macrophytes (duckweed) capability to improve 17% in 15 day. Ten day cultivation of both algae and duckweed showed the highest remediation of Tanjaro River water.

4. Results from the sorghum soil pots experiment showed the decreasing of metals, Fe, Co, Cd, Pb, Cr, As, Cu, Zn, in water sample from Tajaro River during 2 month of the experiment, except Mn which increased individually.
5. The physiochemical measurements of Tanjaro River water showed different values and concentrations in August and September, due to sewage composition were feed the Tanjaro River.
6. Results indicated that irrigation frequency has an effect on metals discharging through the soil column with time. In addition, long-term polluted water irrigation can affect the groundwater quality in the study area.
7. Results of cation and anion concentrations in the discharged water from soil pots show that the irrigation frequencies have a positive effect on ion discharging from the soil column. Cations and anions can reach the ground water by long-term irrigation with Tanjaro River.
8. Results confirmed that, increasing of the irrigation period decreases the value of DO, pH, Ec, TDS, and T in the discharge water from the soil, but increase turbidity.
9. Depending on the BAC for treatments algae and duckweed, showed that; algae has the capability to phycoremediate metals in the order Fe> Mn> Cu> Cr> Co> Zn, while duckweed has ability to phytoremediate metals in the order Fe> Cu> Mn> Cr> Co> Zn, the capacity of duckweed to extract heavy metals is more than algae. Sorghum has ability to phytoremedate metals in the order Zn> Cu> Mn> Co> Cr.
10. The results in the present study concluded that the Tanjaro River can be used for irrigation purposes after passed through the phytotechnology application for long-period.

### 5.3 Recommendations

Based on the previous results and conclusions the following recommendations are made:

1. Direct using of Tanjaro River water for irrigation should be used for those plants that have the ability to accumulate and extract metals from soil solution, where using the Tanjaro River for irrigation, those plants should not be used for human consumptions.
2. The governorate should have plans for recycling (Bioremediation= cost-effective and cheap) Tanjaro River water before being discharged in the Darbandikhan reservoir or used by farmers. Also, this technology should be seen as an economical source for

renewable energy and environmental technology, to extract the biofuel, bioethanol, biodiesel, and for biofertilizer from aquatic macro/microphytes

3. Recommendation to farmers in the Tanjaro area when they use River for irrigation without recycling should be collect the water and save it in the pond to reduce the effect of heavy metals and create the condition for duckweed and algae growth naturally in the pond without any cost especially in the summer season.

## CHAPTER SIX

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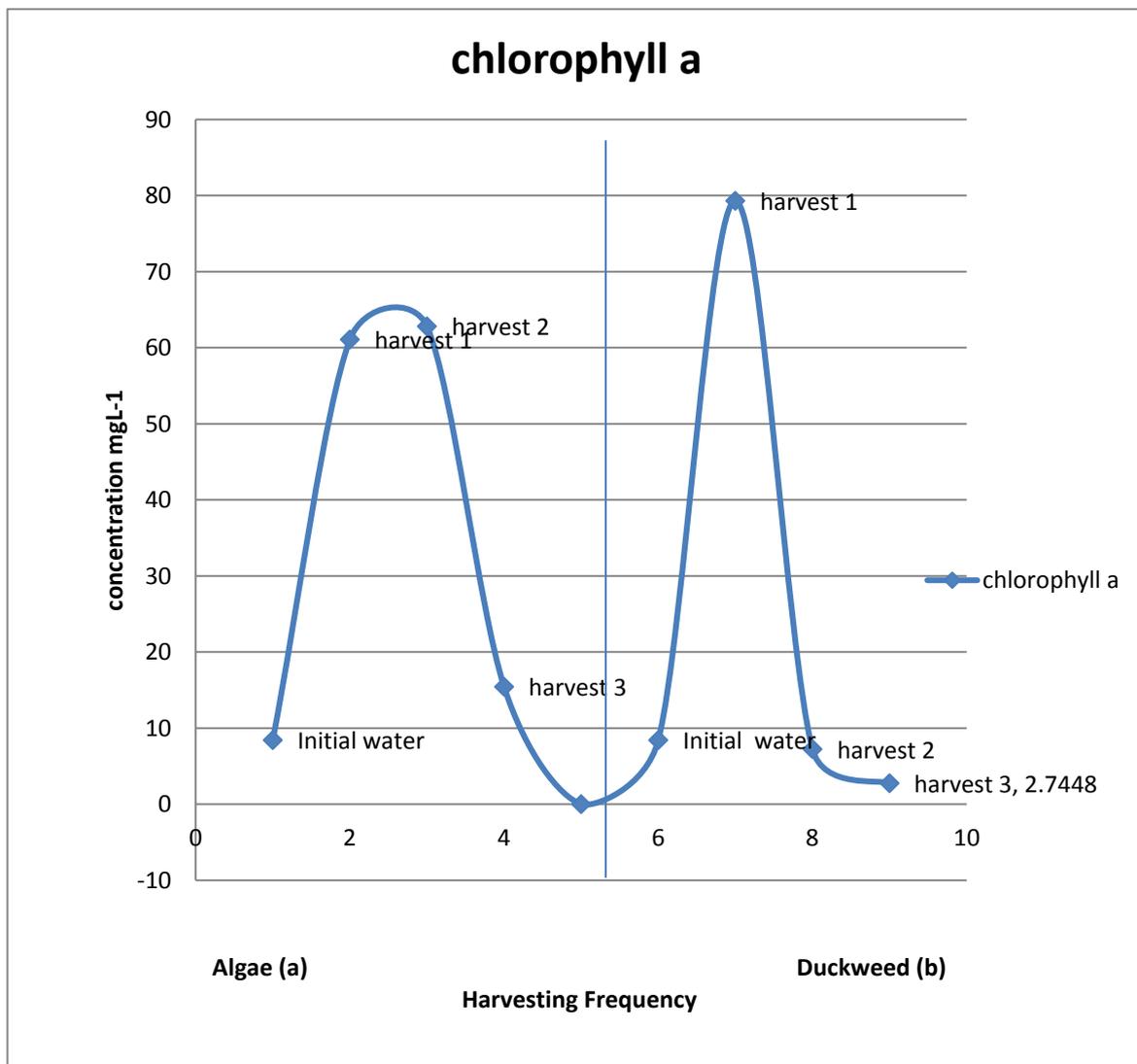
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## CHAPTER SEVEN

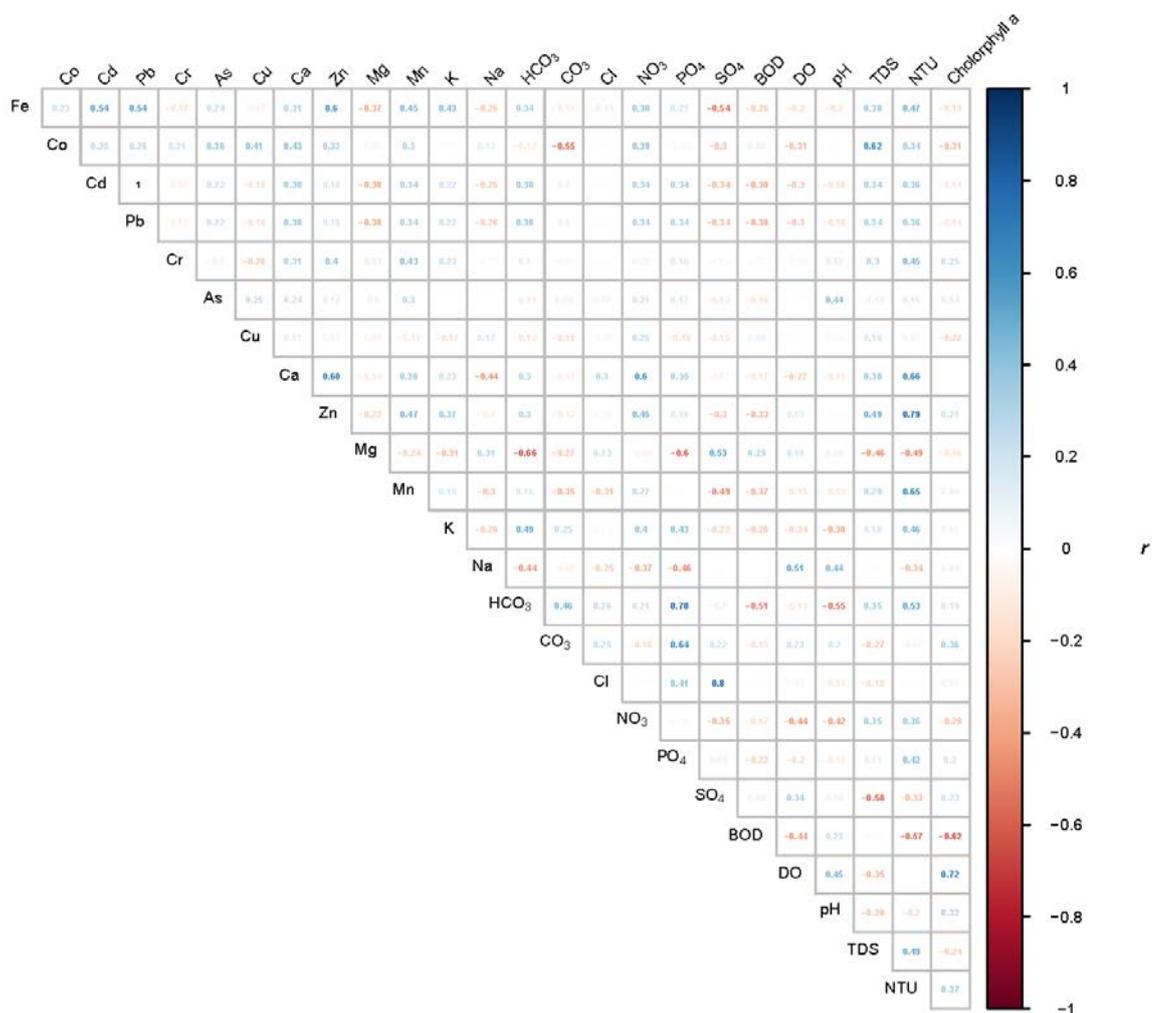
### APPENDIX

**Appendix 1 Correlation coefficient between physiochemical measurements in the algae and duckweed treatment under “Spearman” test at level 0.05**

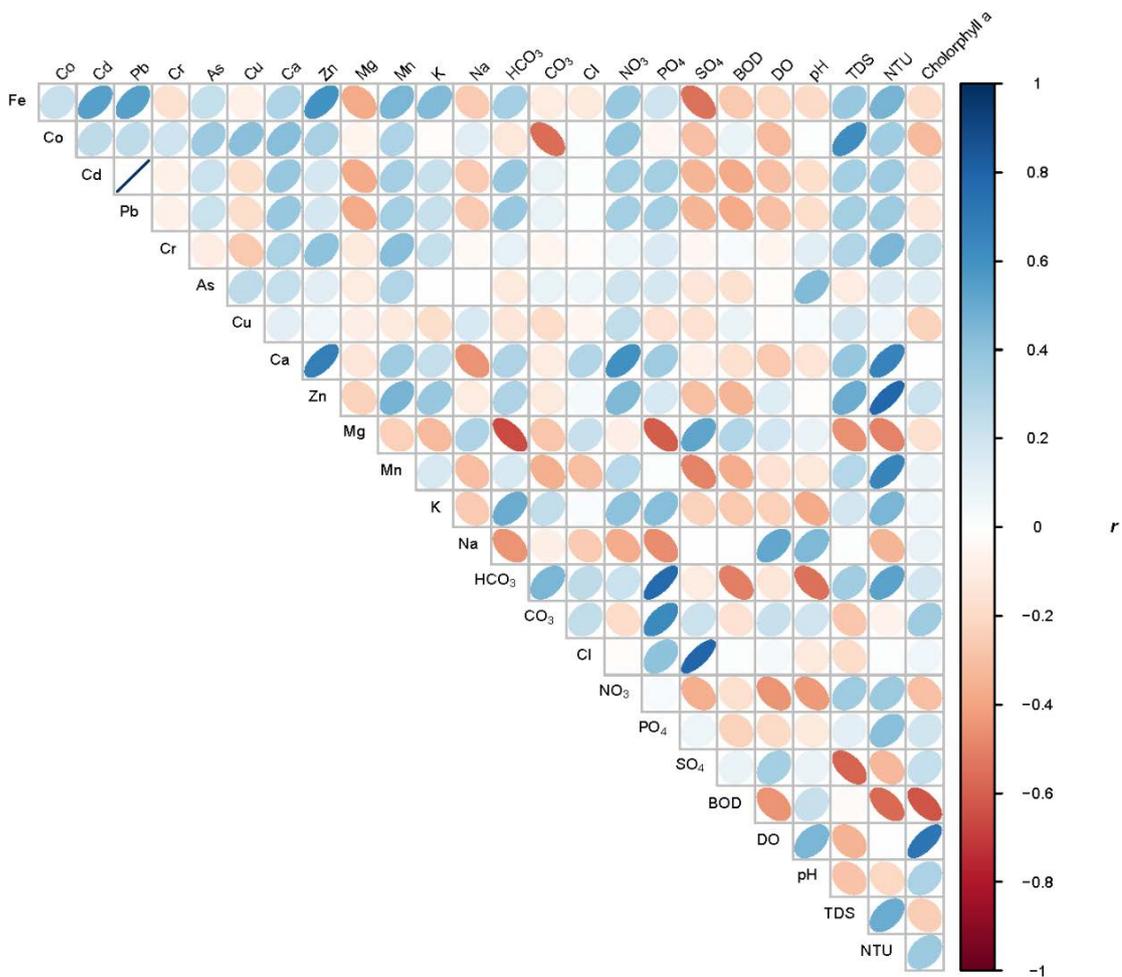
Parameter	Alog alpha	Alog alphase	Abeta	Abetas- e	Dlog alpha	Dlog alphase	Dbeta	Dbetas- e	Arsq	Drsg
Fe mgL <sup>-1</sup>	-3.73	1.47	-0.27	0.16	-1.76	0.68	-0.31	0.07	0.60	0.90
Co mgL <sup>-1</sup>	-4.75	1.04	-0.16	0.11	-3.66	0.18	-0.16	0.02	0.52	0.97
Cd mgL <sup>-1</sup>	-6.71	0.09	-0.02	0.01	-6.71	0.09	-0.02	0.01	0.60	0.60
Pb mgL <sup>-1</sup>	-5.88	0.48	-0.09	0.05	-5.88	0.48	-0.09	0.05	0.60	0.60
Cr mgL <sup>-1</sup>	-5.34	0.72	-0.13	0.08	-4.79	0.36	-0.16	0.04	0.60	0.90
As mgL <sup>-1</sup>	-3.77	0.08	-0.02	0.01	-3.81	0.08	-0.02	0.01	0.73	0.74
Cu mgL <sup>-1</sup>	-4.03	0.54	-0.23	0.06	-3.59	0.09	-0.13	0.01	0.88	0.99
Ca mgL <sup>-1</sup>	4.59	0.48	-0.09	0.05	4.65	0.55	-0.09	0.06	0.61	0.52
Zn mgL <sup>-1</sup>	-0.71	1.07	-0.30	0.11	0.24	0.41	-0.28	0.04	0.78	0.95
Mg mgL <sup>-1</sup>	2.61	0.19	0.04	0.02	2.61	0.23	0.06	0.02	0.71	0.72
Mn mgL <sup>-1</sup>	-2.01	0.04	-0.18	0.00	-2.11	0.22	-0.11	0.02	1.00	0.92
K mgL <sup>-1</sup>	1.88	0.07	-0.05	0.01	1.63	0.21	-0.05	0.02	0.97	0.72
Na mgL <sup>-1</sup>	4.27	0.04	0.00	0.00	4.28	0.05	0.01	0.01	0.43	0.41
HCO <sub>3</sub> mgL <sup>-1</sup>	5.44	0.11	-0.08	0.01	5.22	0.31	-0.10	0.03	0.96	0.82
CO <sub>3</sub> mgL <sup>-1</sup>	3.45	0.14	0.03	0.01	3.05	0.36	-0.11	0.04	0.61	0.79
Cl mgL <sup>-1</sup>	4.31	0.06	0.00	0.01	4.32	0.10	-0.01	0.01	0.01	0.12
NO <sub>3</sub> mgL <sup>-1</sup>	4.12	1.55	-0.40	0.17	2.86	0.59	-0.05	0.06	0.74	0.22
PO <sub>4</sub> mgL <sup>-1</sup>	1.61	0.31	-0.05	0.03	1.64	0.33	-0.18	0.04	0.53	0.93
SO <sub>4</sub> mgL <sup>-1</sup>	4.44	0.06	0.01	0.01	4.43	0.06	0.00	0.01	0.62	0.23
BOD mgL <sup>-1</sup>	1.94	0.52	0.05	0.06	2.02	0.41	0.06	0.04	0.28	0.45
DO mgL <sup>-1</sup>	-0.94	1.59	0.17	0.17	-0.75	1.78	0.14	0.19	0.33	0.21
pH	2.14	0.02	0.00	0.00	2.19	0.04	0.00	0.00	0.56	0.01
TDS mgL <sup>-1</sup>	5.99	0.36	-0.09	0.04	6.01	0.34	-0.07	0.04	0.71	0.67
NTU	4.28	0.34	-0.26	0.04	4.59	0.41	-0.29	0.04	0.96	0.96
chlorophylla mgL <sup>-1</sup>	2.94	0.95	0.04	0.10	3.24	1.24	-0.12	0.13	0.07	0.27



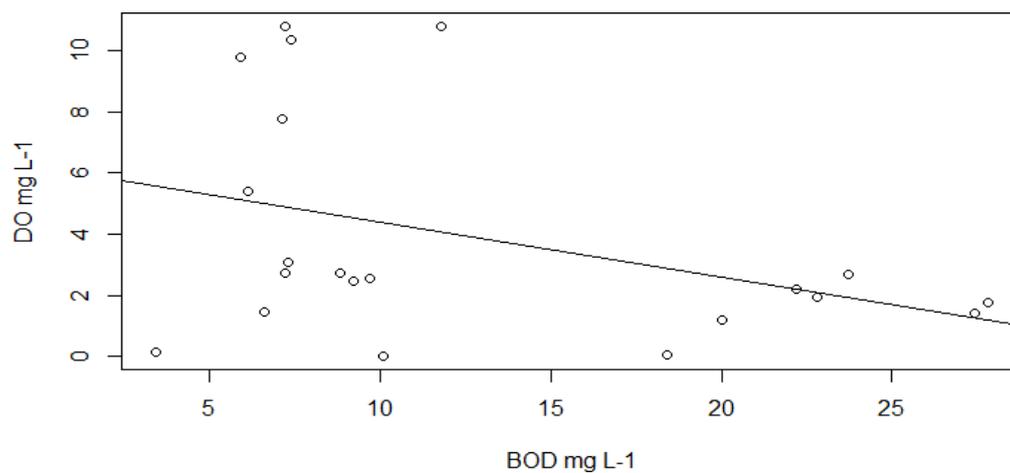
Appendix 2 Chlorophyll *a* concentration mgL<sup>-1</sup>, in the harvesting frequency in (algae and duckweed) aquarium



Appendix 3a Correlation coefficient  $r^2$  between physiochemical measurements



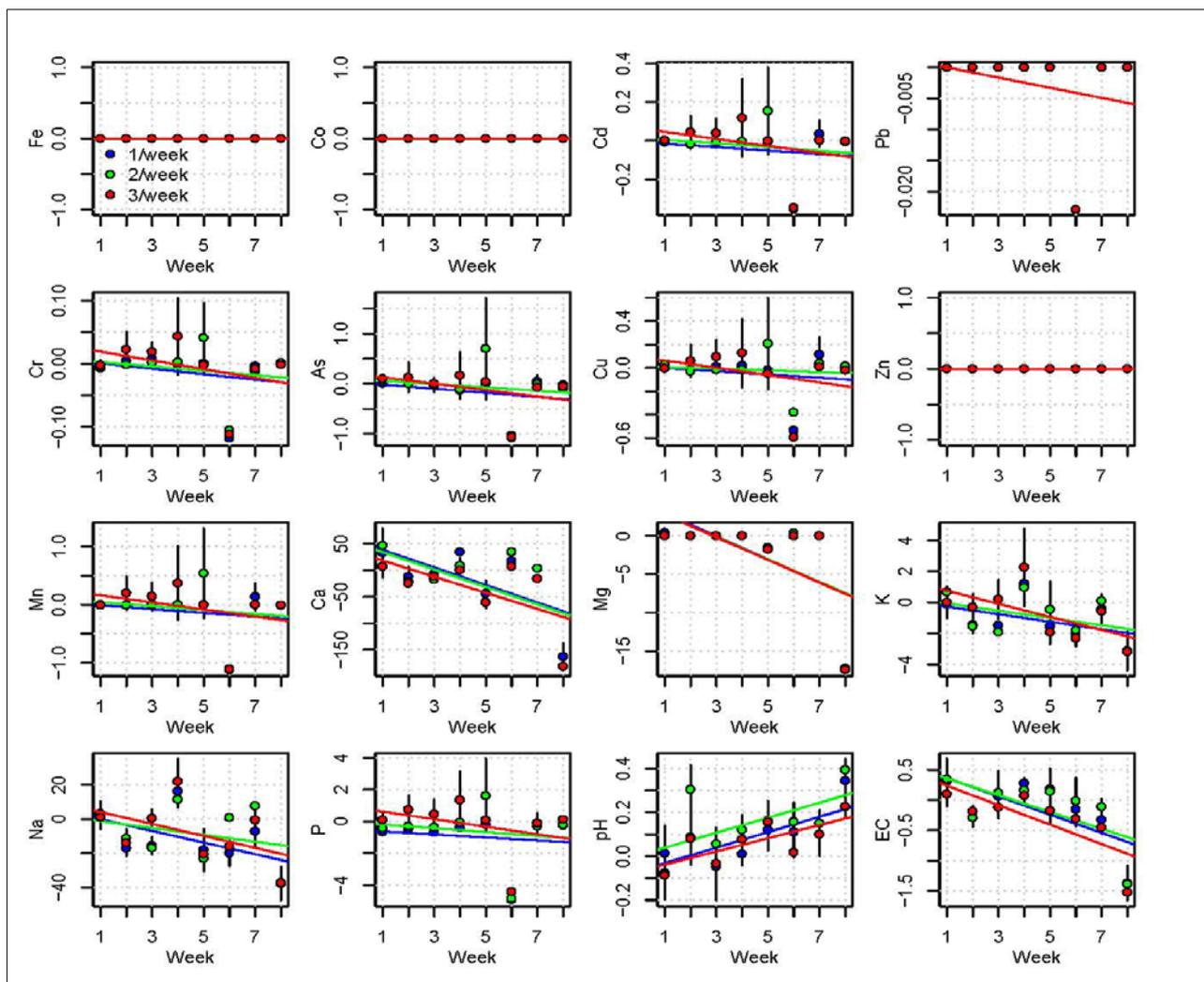
Appendix 3b Relation between physiochemical measurements



Appendix 3c DO regressed against BOD

Appendix 4 Initial soil samples texture

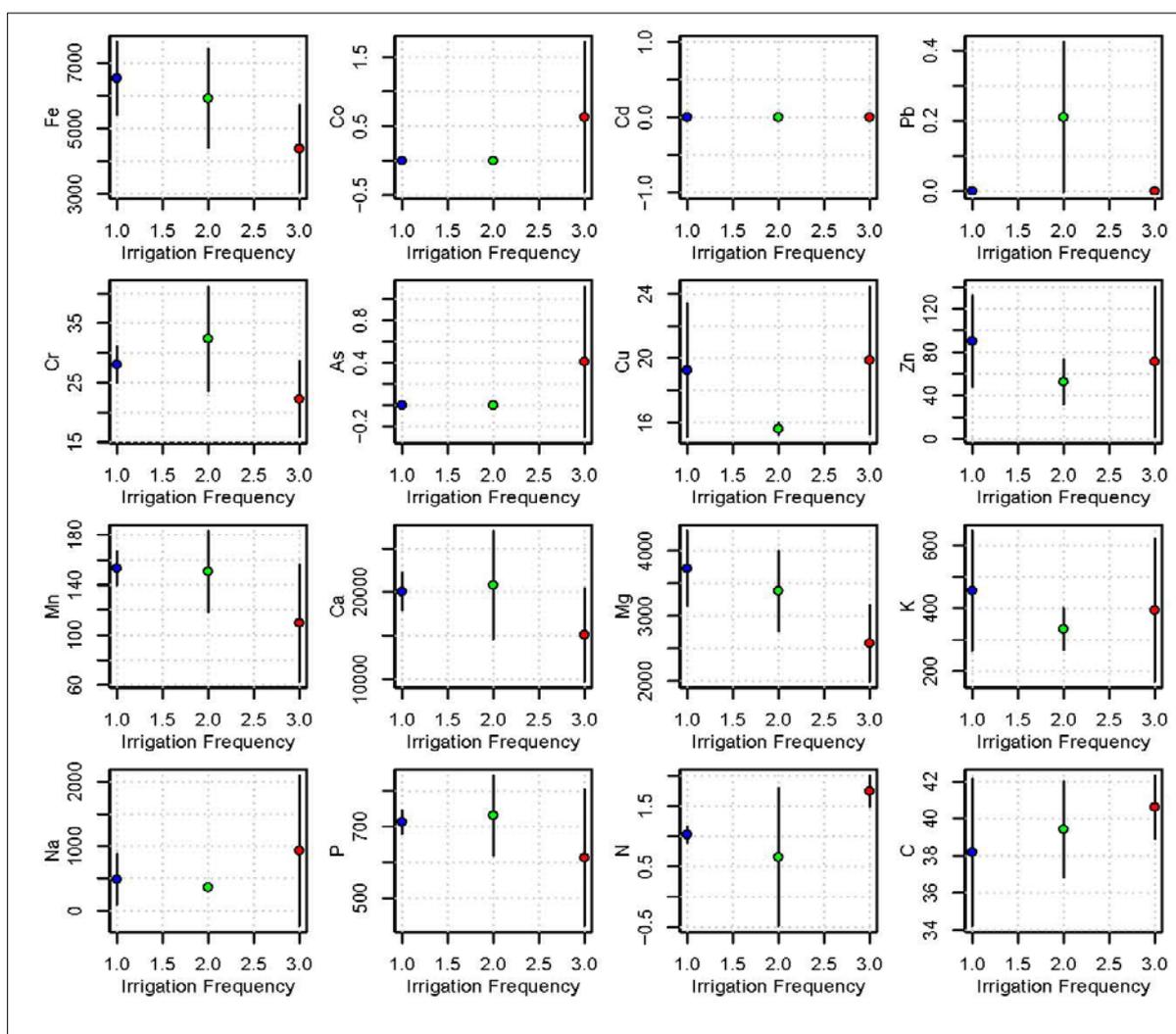
Sand %	Silt %	Clay %	Class
8.3	59.7	32	Silty Clay Loam



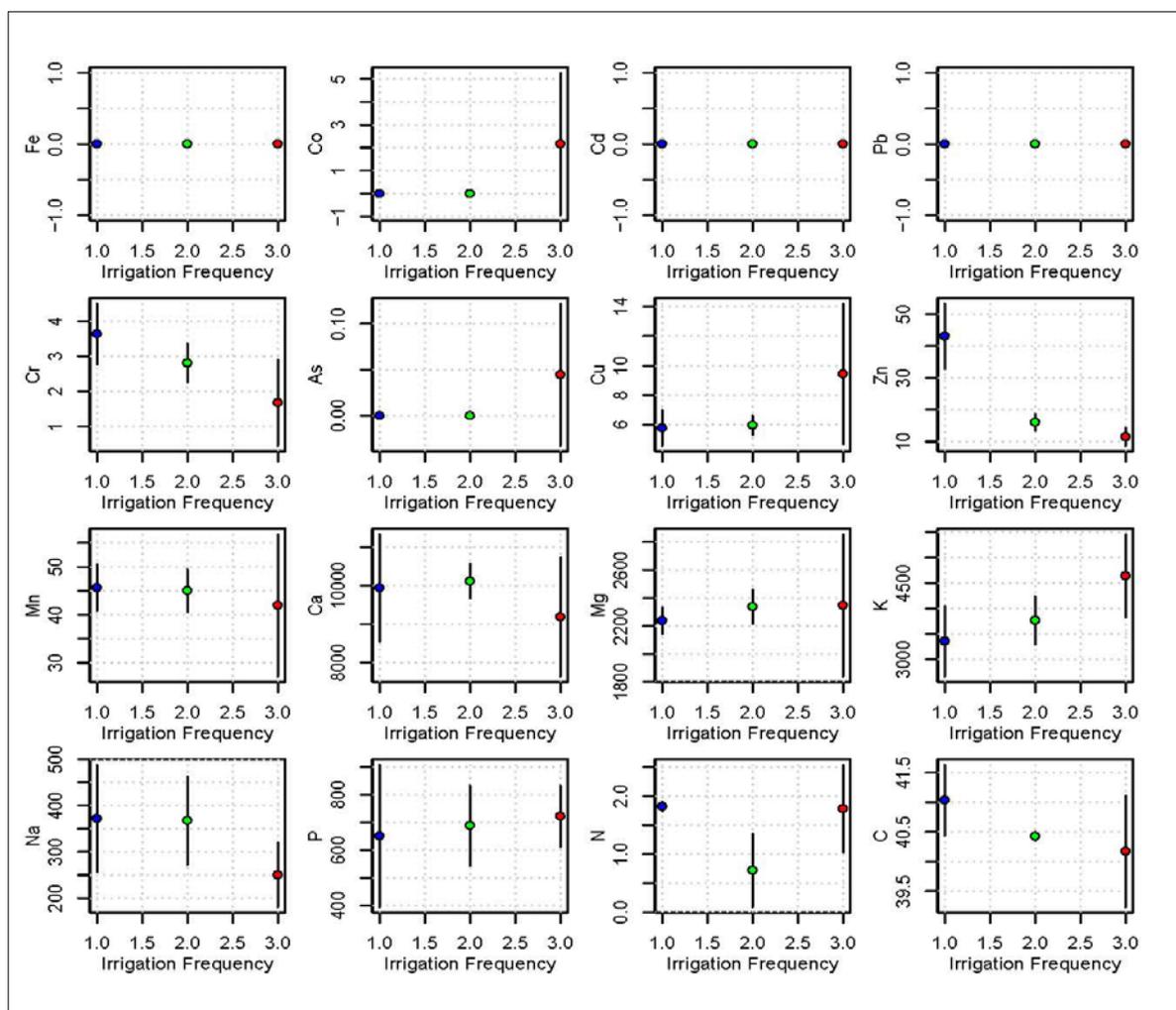
**Appendix 5 Relations between soluble concentration of (Fe, Co, Cd, Pb, Cr, As, Cu, Zn, Mn, Ca, Mg, K, Na, and P mg Kg<sup>-1</sup>) & (pH and EC) in the soil with wastewater irrigation during 9 weeks, under irrigation frequency (1-time/week=blue color, 2-time/week=green color and 3-time/week=red color, by using liner regression coefficient function in R**

**Appendix 6 Increases percentage of soluble metals in the control soil in comparison to initial soil during sorghum experiment**

	Fe	Co	Cd	Pb	Cr	As	Cu	Zn	Mn
<b>Initial Soil mgkg<sup>-1</sup></b>	0.000	0.000	0.102	0.000	0.022	0.226	0.215	0.000	0.294
<b>Irrigated soil (control) mgkg<sup>-1</sup></b>	0.000	0.000	0.132	0.003	0.038	0.355	0.257	0.000	0.424
<b>%increases</b>	0.000	0.000	29.364	0.000	70.484	56.851	19.121	0.000	43.960



**Appendix 7a Relationship between (Fe, Co, Cd, Pb, Cr, As, Cu, Zn, Mn, Ca, Mg, K, Na, and P mg Kg<sup>-1</sup>) & (%N and %C) in the sorghum root, with polluted water irrigation during 9 weeks, under irrigation frequency (1-time/week=blue color, 2-time/week=green color and 3-time/week=red color**



**Appendix 7b Relationship between (Fe, Co, Cd, Pb, Cr, As, Cu, Zn, Mn, Ca, Mg, K, Na, and P mg Kg<sup>-1</sup>) & (%N and %C) in the sorghum shoot, with polluted water irrigation during 9 weeks, under irrigation frequency (1-time/week=blue color, 2-time/week=green color and 3-time/week=red color**

## Appendix 8 Guidelines for interpretation of Water Quality for Irrigation

Parameter	Degree of Restriction of use		
	Slight to Non Severe	Moderate	Severe
Salinity , EC <sub>w</sub> (dS m <sup>-1</sup> )	<0.7	0.7-3.0	>3.0
Total dissolved Solids, TDS	<450	450-2000	>2000
Total suspended solids, TSS	<50	50-100	>100
Bicarbonate, (HCO <sub>3</sub> )	<90	90-500	>500
Chloride (Cl <sub>2</sub> ), total residual	<1.0	1.0-5.0	>5.0
Chloride (Cl),sensitive crops	<140	140-350	>350
Chloride (Cl), sprinklers	<100	100	>100
Boron (B)	<0.7	0.7-3.0	>3.0
Hydrogen Sulfide (H <sub>2</sub> S)	<0.5	0.5-2.0	>2.0
Iron (Fe), drip irrigation	<0.1	0.1-1.5	>1.5
Manganese (Mn), drip irrigation	<0.1	0.1-1.5	>1.5
Nitrogen (N), total	<5	5-30	>30
Sodium (Na <sup>+</sup> ), sensitive crops	<100	100	>100
Sodium (Na <sup>+</sup> ),sprinklers	<70	70	70
Sodium Absorption Ratio SAR	<3.0.0	3.0-9.0	>9.0
Residual Sodium Carbonate RSC	<0	0-2.5	>2.5
Hardness (Grain/gallon )	<200	200-300	>300
Oil and grease	<5.0	5.0	>5.0

Sources: (Ayers and Westcot, 1985).

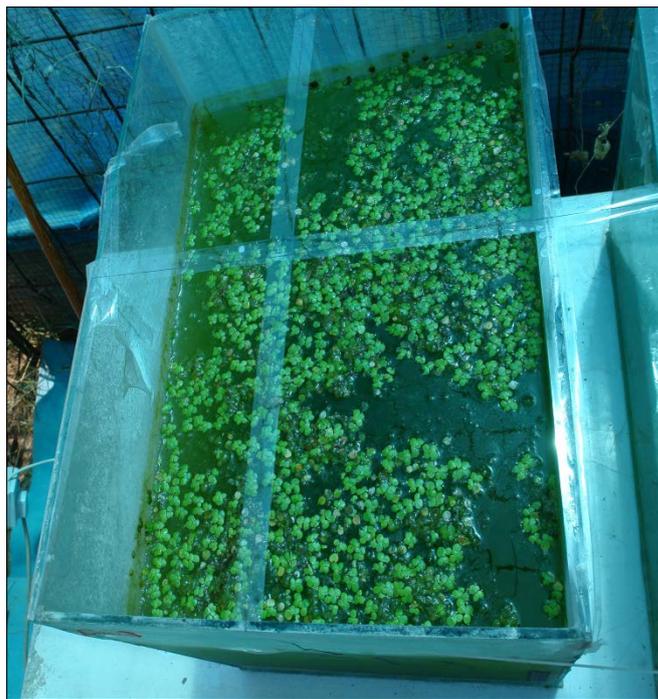
All units in mg.L<sup>-1</sup> unless otherwise noted

**Appendix 9 Guidelines for interpretation of water quality for irrigation (FAO, 1985).**

Potential irrigation problem	Units	Degree of restriction of use		
		None	Slight to moderate	Severe
<b>Salinity</b>				
EC <sub>w</sub>	dS/m	<0.7	0.7-3.0	>3.0
or				
TDS	Mg.L <sup>-1</sup>	<450	450-2000	>2000
<b>Infiltration</b>				
SAR = 0-3 and EC <sub>w</sub>		>0.7	0.7-0.2	<0.2
3-6		>1.2	1.2-0.3	<0.3
6-12		>1.9	1.9-0.5	<0.5
12-20		>2.9	2.9-1.3	<1.3
20-40		>5.0	5.0-2.9	<2.9
<b>Specific ion toxicity</b>				
Sodium (Na)				
Surface irrigation	SAR	<3	3-9	>9
Sprinkler irrigation	Mg.L <sup>-1</sup>	<70	>70	
Chloride (Cl)				
Surface irrigation	Mg.L <sup>-1</sup>	<140	140-350	>350
Sprinkler irrigation	Mg.L <sup>-1</sup>	<100	<100	
Boron (B)				
	Mg.L <sup>-1</sup>	<0.7	0.7-3.0	>3.0
<b>Miscellaneous effects</b>				
Nitrogen (NO <sub>3</sub> -N)	Mg.L <sup>-1</sup>	<5	5-30	>30
Bicarbonate (HCO <sub>3</sub> )	Mg.L <sup>-1</sup>	<90	90-500	500
pH	unit		Normal range 6.5-8.4	



**Appendix 10 Duckweed Cultivation in 5 day**



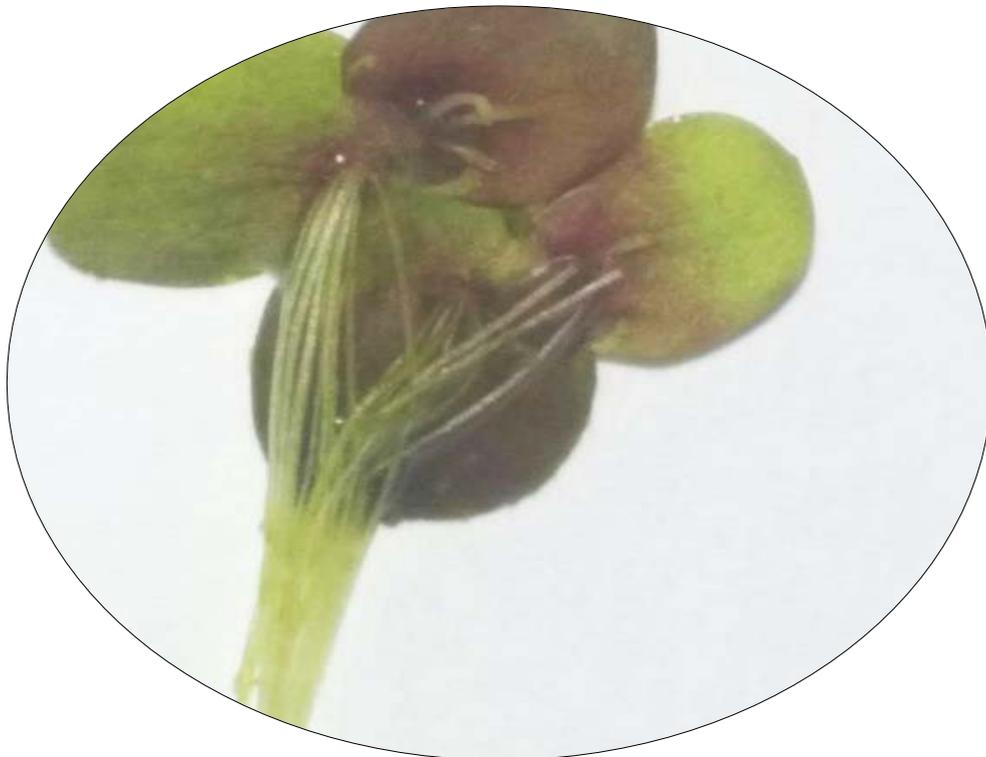
**Appendix 11 Duckweed in 10 of cultivation**



**Appendix 12 Duckweed collection from Tanjaro River**



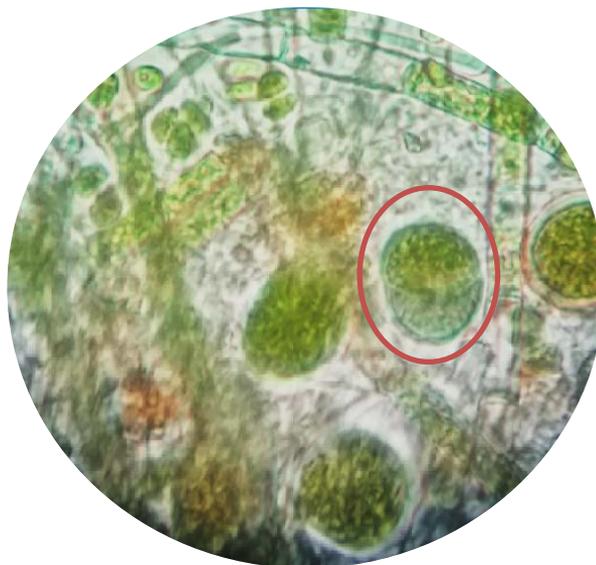
**Appendix 13a Duckweed leaf examinations under microscope 4X**



**Appendix 13b Duckweed root examination under microscope 40X**



Appendix 14 Algae culturing in the Lab.



Appendix 15a Algae *chroococcus* sp examination under Lambomed Digiplus microscope 100X oil



**Appendix 15b Algae examination Lambomed Digiplus microscope 100X oil**



**Appendix 15c Algae *Oscillatoria sp* examination under Lambomed Digiplus microscope 100X oil**



**Appendix 15d Algae *Oedogonium Sp* examination under Lambomed Digiplus microscope 100X oil**



**Appendix 15e Algae *Oedogonium*; Oogonium and egg examination under Lambomed Digiplus microscope 100X oil**



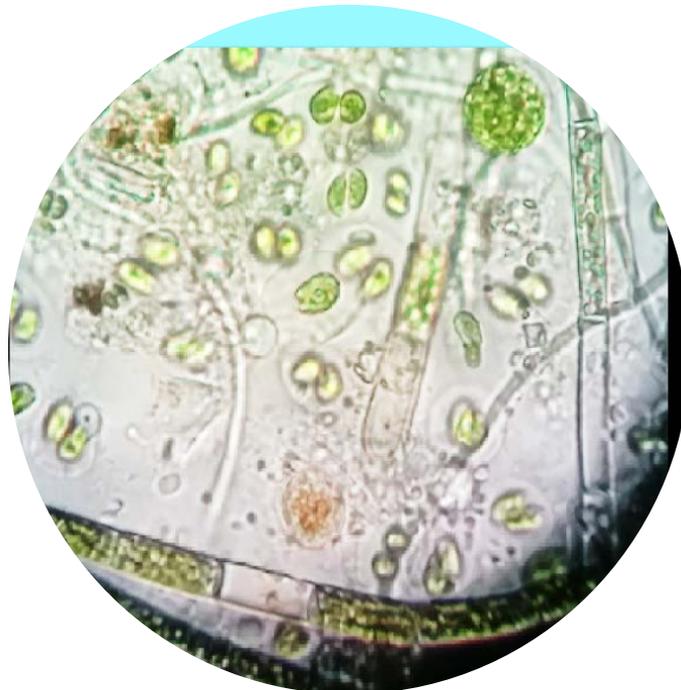
Appendix 15f Algae examination under Lambomed Digiplus microscope 100X oil



Appendix 15g Algae *Scenedesmus sp* examination under Lambomed Digiplus microscope 100X oil



**Appendix 15h Algae examination under Lambomed Digiplus microscope 100X oil**



**Appendix 15i Algae examination under Lambomed Digiplus microscope 100X oil**



حكومة إقليم كردستان  
الوزراء تعليم العالي و البحث العلمي  
الجامعة السلیمانیة  
الكلية العلوم الهندسة الزراعية

# استخدام الذرة البيضاء و الطحالب المائية لتحسين نوعية مياه نهر تانجارو ملوثة للاغراض الري

رسالة

مقدمة الى مجلس كلية الزراعة للعلوم الهندسية في جامعة السلیمانیة كجزء من متطلبات  
نيل شهادة دكتورا في علوم التربة والمياه

(تلوث البيئية)

من قبل

ژینۆ خالد محمد

بكالوريوس في علوم التربة والمياه (٢٠٠٤) ، جامعة السلیمانیة

ماجستير في تلوث البيئية (٢٠١١) ، جامعة السلیمانیة

باشراف

د. دانیال هیرماس

استاذ

د. خسرو عبدالله رشد

استاذ

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## الخلاصة

استخدام الطريقة النباتية لتقييم قدرة كل من (الطحالب، الطحلب البطي ونبات الذرة الرفيعة) لمعالجة مياه الصرف الصحي في نهر تانجرو وإعادة استخدامها لأغراض الري، كذلك أظهرت النتائج قدرة كل من الطحالب، الطحلب البطي على تصفية مياه الصرف الصحي في نهر تانجرو من المعادن الثقيلة مع المكونات الكيميائية والفيزيائية مثل:  $T^{\circ}c$ , pH, DO, BOD, TDS, Ec, Turbidity and chlorophyll *a*,  $NO_3^-$ ,  $PO_4^{3-}$ ,  $SO_4^{2-}$ ,  $HCO_3^-$ ,  $CO_3^{2-}$ ,  $Cl^-$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Na^+$ ,  $K^+$ ,  $Fe$ ,  $Co$ ,  $Cd$ ,  $Pb$ ,  $Cr$ ,  $Cu$ ,  $Zn$  and  $Mn$  حيث أظهرت قيمة المكونات الكيميائية والفيزيائية اختلافات كبيرة قبل التجربة وبعد التجربة، وانخفضت قيمها لتصفية المياه بعد استخدام الطحالب والطحلب البطي باستثناء (DO و chlorophyll *a*) التي أظهرت زيادة في القيمة، وكانت نسبة تقليل الأيونات الموجبة والسالبة لكل من الطحالب والطحلب البطي على النحو التالي: (100%) لكل من ( $K^+$ ,  $As$ ,  $Cr$ ,  $Pb$ ,  $Cd$ ,  $Fe$ ) والتي سجلت انخفاضاً، وعلى الرغم من ذلك أظهرت الطحالب كفاءة عالية على تقليل ( $Mn$ ,  $Zn$ ,  $Cu$ ,  $Co$ ,  $NO_3^-$ ) بالمقارنة مع الطحلب البطي، من ناحية أخرى، تميّز الطحلب البطي بالقدرة على تقليل ( $CO_3^{2-}$ ,  $HCO_3^-$ ,  $Cl^-$ ,  $PO_4^{3-}$ ) من مياه الصرف الصحي في نهر تانجرو.

قيمة (IWQI) كانت (12) وهي تصنف في الفئة المياه منخفضة للري الزراعي، ولكن بعد معالجتها بالطحالب والطحلب البطي ارتفعت القيمة الى (13 و 14) على التوالي. وأظهرت النتائج ارتفاع قيمة (IWQI). وكذلك خلصت النتيجة إلى أن الطحالب لديها القدرة على تحسين (8%) من 50 لتر من المياه في 15 يوماً من الري، والطحلب البطي لديه القدرة على تحسين (17%).

وخلصت نتائج أخذ عينات مياه الري من نهر تانجرو خلال تجربة الذرة الرفيعة من شهر (آب - تشرين الأول) إلى أن قيمة المكونات الكيميائية والفيزيائية أظهرت اختلافات كبيرة بين عينات المياه المأخوذة مباشرة من نهر تانجرو والعينات التي تم تخزينها في الخزان لمدة 7 أيام، وفي الوقت نفسه ظهرت اختلافات كبيرة في مكونات المياه طيلة فترة تلك الأشهر، والسبب في ذلك يعود الى تركيب مياه الصرف الصحي لمدينة السليمانية.

أظهرت نتائج تجربة الذرة الرفيعة، وتكرار الري بمياه الصرف الصحي لنهر تانجرو، تأثيرات إيجابية على كيمياء التربة، وتفريغ المعادن الثقيلة والمواد المغذية للنبات من تربة الأواني أثناء تجربة الذرة الرفيعة. وبهذا تُظهر لنا هذه النتائج أن تكرار الري له تأثير على المعادن التالية: ( $Fe$ ,  $Co$ ,  $Cd$ ,  $Pb$ ,  $Cr$ ,  $As$ ,  $Cu$ ,  $Zn$  and  $Mn$ ) ملغم كغم<sup>-1</sup>) التي يتم تفريغها عبر التربة مع مرور الوقت، وهذا يؤكد لنا بأن استخدام مياه الصرف الصحي للري على المدى الطويل يؤثر على المياه الجوفية.

وأظهرت نتائج الأيونات الموجبة ( $Ca^{2+}$ ,  $Mg^{2+}$ ,  $K^+$  و  $Na^+$ ) والأيونات السالبة ( $HCO_3^-$ ,  $CO_3^{2-}$ ,  $NO_3^-$ ,  $PO_4^{3-}$ ) وهـ ( $SO_4^{2-}$ ) في الماء الذي تم تصريفه؛ بأن لتكرار الري تأثير إيجابي على تصريف الأيونات الموجبة والسالبة وتفريغها في التربة، وخاصة عند استخدام مياه الصرف الصحي للري، فإن الأيونات الموجبة والسالبة قادرة على أن تصل إلى المياه الجوفية. وأكدت النتيجة نقص قيمة (DO pH, Ec, TDS و T) في المياه المترشحة الى التربة، باستثناء نسبة التعكر في الماء المترشح الذي شهد زيادة خلال التجربة.

أظهرت نتائج تأثيرات الري بالمياه العادمة على كيمياء التربة العلاقة السلبية بين تواتر الري وإجمالي المعادن الثقيلة، ولم تسجل أية اختلافات بين أوقات عمليات الري خلال مدة 9 أسابيع من التجربة، باستثناء الرصاص (pb) الذي أظهر اختلافات بين تواتر الري (1، 2، 3 مرات للري/ أسبوع). وتم تقليل التركيز الكلي للمعادن الثقيلة في التربة أثناء التجربة، بسبب امتصاصها من قبل الذرة الرفيعة وترشحها الى التربة. كما انخفض تركيز الأيونات الموجبة ( $Mg^{2+}$  و  $Ca^{2+}$ ) في التربة أثناء التجربة، ولم يُظهر تكرار الري اختلافات مهمة في تركيز الأيونات الموجبة ( $Mg^{2+}$  و  $Ca^{2+}$ ). من ناحية أخرى، تأثر تركيز كل من ( $Na^+$  و  $K^+$ ) بسبب تواتر الري، حيث شهد زيادة التركيز في التربة في (1 و 2 مرة للري/ أسبوع) وانخفاض التركيز في التربة في (3 مرات للري/ أسبوع).

وتم زيادة نتائج التركيز الكلي P المتأثر بتواتر الري في التربة عند (1 و 2 مرة للري/ أسبوع) وانخفضت عند الري لمدة (3 مرات للري/ أسبوع). وانخفضت النسبة الكلية للنيتروجين (N) في التربة، كما ارتفعت النسبة الكلية للكربون (C) في التربة أثناء تجربة الذرة الرفيعة، وكان هناك فرق كبير بين تكرار الري لكل من (% C و % N).

أظهرت النتائج بأن الذرة الرفيعة لديها القدرة على امتصاص المعادن الثقيلة والمغذيات الموجودة في الجذر أكثر من الأجزاء المخضرة، كما أن هناك اختلافات كبيرة بين تردد الري في المعادن وتراكيز المغذيات في جذر الذرة الرفيعة، باستثناء (K، Cu، Pb، Cd) التي لم تظهر أية اختلافات مهمة. من ناحية أخرى، أظهرت تراكيز المعادن والمواد المغذية في الأجزاء الخضراء من الذرة الرفيعة فروقا منخفضة بين ترددات الري أثناء التجربة.

نتائج نقص وزيادة نسبة المعادن في التربة بعد الري بمياه الصرف الصحي خلال تجربة الذرة الرفيعة، تظهر النسبة المئوية للمعادن المتزايدة في التربة التي لم تزرع فيها الذرة الرفيعة (تحكم)، وترتيب الزيادة هو كالتالي (Pb>Cr>Cd>Cu>As>Mn)، ما عدا (Fe، Co، Zn) بالمقارنة مع محتوى المعادن في التربة الأولية.

وخلصت النتائج إلى أنه عندما تم ري التربة بواسطة مياه الصرف الصحي من نهر تانجرو، كان سبباً لتراكم المعادن في التربة.

اتخاذ قرار بالاعتماد على (BAC) حول قدرة كل من: (الطحالب، الطحلب البطي والذرة الرفيعة) على معالجة وتصفية مياه الصرف الصحي؛ أظهرت أن الطحالب لديها القدرة على معالجة المعادن (Zn>Co>Cr>Cu>Mn>Fe) على الترتيب، كما أن الطحلب البطي قادر على معالجة المعادن (Zn>Co>Cr>Mn>Cu>Fe)، ولنبات الذرة الرفيعة القدرة على معالجة المعادن (Cr>Co>Mn>Cu>Zn). من ناحية أخرى، لا تستطيع (الطحالب، الطحلب البطي والذرة الرفيعة) معالجة المعادن (As، Pb، Cd) في الماء اعتماداً على  $BAC < 1$ ، كما وأن قيمة الذرة للحديد (Fe) كانت  $BAC < 1$  مقارنةً بالطحالب والطحلب البطي، وأن قدرة الطحلب البطي على تصفية ماء تانجرو من المعادن الثقيلة كانت أكثر من الطحالب والذرة الرفيعة.

وخلصت نتائج هذه الدراسة لمعالجة ماء نهر تانجرو إلى أن: وجوب معالجة مياه نهر تانجرو بالطحالب والطحلب البطي قبل استخدامها كمصادر للري. بالإضافة إلى ذلك، وإذا استخدمت المياه العادمة مباشرة كمصدر للري فلنكن لتلك الأنواع من النباتات التي لا تدخل كمصادر للوجبات اليومية للإنسان، مثل نبات الذرة الرفيعة. كما وإن الاستخدام المستمر لمياه نهر تانجرو للري بدون اتخاذ طرق لمعالجته وتصفيته له آثار ضارة على التربة والنبات والمياه الجوفية، وهناك حاجة ماسة للبحث والرصد سنويًا.



حۆكومهتی هه‌ریمی كوردستان  
وهزارهتی خویندنی بآاو توێژینه‌وهی زانستی  
زانكۆی سلیمانی  
كۆلیجی زانسته نه‌ندازیارییه كشتوكالیه‌كان

# به‌كار هینانی روه‌کی گسک و چه‌ن جووری قه‌وزه‌و گیا مراوی بو باشکردنی پیکهاته‌ی ئاوی پیسبوی روبری تانجه‌رو بو ئاودی‌ری

تیژیکه

پیشکەش کراوه به نه‌نجومه‌نی کۆلیجی نه‌ندازیاری زانسته کشتوكالیه‌كان له زانكۆی  
سلیمانی، وه‌ك به‌شیک له پیداو‌یستی به‌ده‌ست هینانی پروانامه‌ی دکتورا له

زانستی خاک و ئاو

(پیسبونی ژینگه)

له‌لایه‌ن

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همروه‌ها نهنجامی نایونه موجهبه‌کانی (  $Na^+$  و  $K^+$  ،  $Ca^{2+}$  ,  $Mg^{2+}$  ) له‌گه‌ل نایونه سالبه‌کان ( $HCO_3^-$  ,  $CO_3^{2-}$  ,  $NO_3^-$ ) له‌نیو ئاوی داچۆراوی خاکه‌که‌دا، پیشانیدا که چند چاره‌ی ئاودانه‌کان کاریگه‌ریکی نهرینی همیه له‌سه‌ر همیه‌ک نایونه موجهب و سالبه‌کان که دابچۆرین له نیو خاکه‌که‌دا ، له‌کاتیکدا که نایکی نه‌گنجاو به‌کاربه‌نهریت بۆ ئاودان وه نایونه سالب و موجهبه‌کان توانای ئه‌مه‌یان همیه بگه‌نه ئاوی ژیر زه‌وی . نهنجامی همیه‌ک له به‌های ( DO pH, Ec, TDS ) کهمی کرد له‌نیو ئاوی داچۆراوی خاکه‌که‌دا بیجگه له به‌های ئیلی ئاوی داچۆراو زیادبونی تومار کرد له‌ماوه‌ی تاقیکردنه‌وه‌که‌دا.

ده‌نه‌نجامی هه‌لسه‌نگاندنی کاریگه‌ری ئاودیری به‌ئاوی روبراری تانجاو له‌سه‌ر پیکهاته کیمیاویه‌کانی خاک پیشانیدا، که په‌یوه‌ندییه‌کی نهرینی همیه له نیوان چندجاره‌ی ئاودانه‌کان له‌گه‌ل په‌یتی گشتی کانزا قورسه‌کان، له‌همه‌مان کاتدا هیچ جیاوازییه‌ک تومار نه‌کرا له‌نیوان چندجاره‌ی ئاودانه‌کان خویاندا بۆ ماوه‌ی نو هه‌فته له‌م توژی‌ینه‌وه‌یه‌دا، بیجگه له pb که جیاوازی هه‌بوو له‌نیوان چندجاره‌ی ئاودانه‌کانی (3، 2، 1 جار ئاودان / هه‌فته). په‌یتی گشتی کانزا قورسه‌کان له خاکه‌که‌دا که‌میان کرد به هۆی هه‌لمژینیان له‌لایهن روه‌کی گسکه‌وه داچۆرانیان به‌نیو خاکه‌که‌دا . همروه‌ها په‌یتی همیه‌ک له‌نایونه موجهبه‌کانی (  $Ca^{2+}$  و  $Mg^{2+}$  ) که‌میان کرد له‌نیو خاکه‌که‌دا له‌ماوه‌ی توژی‌ینه‌وه‌یه‌که‌دا له‌گه‌ل ئه‌مه‌شدا چندجاره‌ی ئاودانه‌کان هیچ جیاوازییه‌کیان پیشان نه‌دا له‌سه‌ر په‌یتی نایونه موجهبه‌کان (  $Ca^{2+}$  و  $Mg^{2+}$  )، له‌لایه‌کی تروه‌ه په‌یتی همیه‌ک له (  $K^+$  و  $Na^+$  ) کاریگه‌رییان له‌سه‌ر بوو به‌هۆی چندجاره‌ی ئاودانه‌کانه‌وه که‌له ( 1 و 2 جار ئاودان/هه‌فته) په‌یتی‌که‌میان زیادی کرد له خاکه‌که‌دا، بلام له (3 جار ئاودان /هه‌فته ) کهمی کرد. نهنجامی په‌یتی گشتی P له‌نیو خاکه‌که‌دا که کاریگه‌ری له‌سه‌ر بوو به هۆی چند جاره‌ی ئاودانه‌کان، که په‌یتی‌که‌ه‌ی زیادیکرد له همیه‌ک ( 1 و 2 جار ئاودان/هه‌فته) که‌میکرد له (3 جار ئاودان/هه‌فته)، ریژه‌ی گشتی نایترۆجین (N) کهمی کرد له خاکه‌که‌دا، هاوکات ریژه‌ی گشتی کاربۆن (C) زیادی کرد له خاکه‌که‌دا له‌ماوه‌ی توژی‌ینه‌وه‌ی گسکه‌که‌دا همروه‌ها جیاوازی هه‌بوو له‌نیوان چند جاره‌ی ئاودانه‌کان بۆ همیه‌ک له ( %C و %N ).

له‌ توژی‌ینه‌وه‌ی گسکه‌که‌دا ده‌رکه‌وت روه‌کی گسک توانای زیاتر کۆکردنه‌وه‌ی کانزا قورسه‌کان و ماده خۆراکییه‌کانی همیه له به‌شی ره‌گه‌هیدا وه‌ک له به‌شه سه‌وزه‌که‌ی ، همروه‌ها جیاوازییه‌کی زۆریش به‌دی‌کرا له نیوان چند جاره‌ی ئاودانه‌کان و په‌یتی کانزاکان له نیو ره‌گی گسکه‌که‌دا، جگه له (K، Cu، Pb، Cd) هیچ جیاوازییه‌کی نیشان نه‌دا . له‌لایه‌کی تروه‌ه په‌یتی کانزاکان و ماده خۆراکییه‌کان له‌به‌شی سه‌وزه‌گی گسکه‌که‌دا جیاوازییه‌کی زۆر که‌م هه‌بوو له نیوان چندجاره‌ی ئاودانه‌کان به‌دریژیایی توژی‌ینه‌وه‌که.

ده‌نه‌نجامی که‌م بوون و زیادبونی کانزاکان له نیو خاکه‌که‌دا له‌ئاوی ئاودان به‌ئاوی روبراری تانجاو له‌ماوه‌ی توژی‌ینه‌وه‌ی گسکه‌که‌دا ده‌رکه‌وت که ریژه‌ی کانزاکان له‌ئاو خاکه‌که‌دا زیادکردبوو که گسکی تیا نه‌رویندراوو (کۆنترۆل)، وه‌همروه‌ها زنجیره‌ی زیادبونی کانزاکان به‌م شویه‌یه بوو (Pb>Cr>Cd>Cu>As>Mn) بیجگه‌له Fe، Co، Zn به به‌راوردکردن له‌گه‌ل کانزاکان له‌ئاو خاکی سه‌ره‌تای پنبش چاندنه‌که‌دا، همروه‌ها ده‌نه‌نجامی توژی‌ینه‌وه‌ی گسکه‌که‌ه‌ی ده‌ری خست له‌کاتی ئاودانی خاک به‌ئاوی تانجاوه‌وه هۆکاریک ده‌بیت بۆ کۆبونه‌وه‌ی کانزا قورسه‌کان له نیو خاکه‌که‌دا.

بریاردان له‌سه‌ر توانای همیه‌ک له قه‌وزه ، گیامراوی و روه‌کی گسک بۆ پاکردنه‌وه‌ی ئاوبرووباری تانجاو له‌سه‌ر به‌مه‌ی BAC به‌م شویه‌یه بوو که قه‌وزه توانای پاککردنه‌وه‌ی ئاوی همیه بۆ همیه‌ک له‌م کانزایانه به زنجیره‌ی (Zn>Co>Cr>Cu>Mn>Fe) ، همروه‌ها گیامراوی توانای همیه بۆ پاککردنه‌وه‌ی کانزاکان

(Zn>Cu>Mn>Co>Cr) گسک توانای پاککردنهوهی کانزاکانی (Fe>Cu>Mn>Cr>Co>Zn) ههیه . له لایهکی ترهوه ، ههیهکی له قهوزه گیا مراوی و گسک نهیانتوانوه کانزاکانی (Cd،Pb،As) له ئاوهکهدا لابرن لهسهه بنهمای  $BAC < 1$  . ههروهها بههای  $BAC < 1$  گسک بۆ کانزای Fe به بهراورد به قهوزه و گیامراوی . ههروهها گیامراوی توانای کهمکردنهوهی پهیتی کانزاقورسهکانی له ئاوبرووباری تانجهرۆدا زیاتر بوو بهبهراورد به قهوزه و گسک .

دهرئهنجامی ئهم توئیزینهوهیه بۆ پاککردنهوهی ئاوی روبراری تانجهرۆ، پیمان دهلتیت که پئویسه ئاوی روبرارهکه پئیش بهکارهینانی راستهوخوی بۆ ئاودیری مامهلهی پئیکری بهقهوزه و گیامراوی ، ئهگهر راستهوخۆ بهکارهینرا بۆ ئاودان بۆ ئهوجۆره روهکانه بهکاربهیت که ناچنه زنجیرهی خۆراکی رۆژانهی مروفهوه ، بۆ نمونه گسک . بهکارهینانی بهردهوامی روبراری تانجهرۆ له ناوچهی تانجهرۆ بۆ ئاودان بهی بهکارهینانی ریگهی پاکسازی دهپهته هۆکاریک بۆ زیان گهاندن به پیکهاتهی خاک و رووهک و ئاوی ژیر زهوی، وه پئویستی به چاودیری وتوئیزینهوهی سالانه ههیه .