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HEAVY METALS BIO-ADSORPTION BY *HIBISCUS SABDARIFFA L.* FROM CONTAMINATED WATER

The metal biosorption is the removal of metal ions by inactive, nonliving biomass due to highly attractive forces present between them. Bio-adsorption capacity of *Hibiscus sabdariffa L.* commonly known as Roselle or red sorrel purchased from Fenoj region in Sistan province in the south-eastern region of Iran in a batch system of waste water by considering the effects of various parameters like initial concentration, pH, contact time, temperature, agitation speed and bio-adsorbent dose were studied. According to boost the capacity of bio-adsorption black tea residue was added to the red tea residue by different concentrations and percentages. Effect of various pH; temperature; dose of red tea residue in accompany by of black tea residue after infusion of 10 minutes in contaminated waste water solution in different contact time and initial concentration, particle size and agitation speed were studied. The samples were analyzed by standardized international protocols in Nutrition and Food Sciences Research Center in Pharmaceutical Sciences Branch, Islamic Azad University. The best results obtained by 0.5 % of red tea + 3 % black tea residues after 40 minutes. Further increase in contact time more than 40 minutes did not show significant increase in bio-adsorption ($p > 0.05$). The results of current study revealed, that using 0.5 % red tea residue in accompany by 3 % black tea residue can remove and decrease cadmium and nickel significantly and for cobalt decreasing the rate of adsorption is not as much as 2 other metals but remove cobalt after 40 minutes in remarkable contents.

Keywords: Bio-adsorption; red tea residue; black tea; heavy metals; contaminated water.

1. Problem statement.

Since 1990, 2.6 billion people have benefitted from improved drinking water, but 663 million people worldwide are still without appropriate access to such sources (Nriagu, 1979). As one of its Sustainable Development Goals, the UN aims to achieve universal and equitable access to safe and affordable drinking water for all by 2030. At the Summit of 25–27 September 2015, the 193-member states of the United Nations adopted a joint program for sustainable development after 2015, which includes universal access to water and sanitation by 2030, And better management of water resources. Targets of Sustainable Development Objective are summarized as following:

- by 2030, ensure universal and equitable access to safe drinking water at an affordable cost;
- by 2030, ensure equitable access to adequate sanitation and hygiene services for all and to put an end to open defecation, paying particular attention to the needs of women and Girls and vulnerable people;
- improve water quality by reducing pollution by eliminating the dumping of wastes and minimizing emissions of chemicals and hazardous materials by 2030 by halving the proportion of water Untreated wastewater and considerably increasing the recycling and safe reuse of water globally (UN-Water, 2016).

- by 2030, significantly increase the rational use of water resources in all sectors and ensure the sustainability of withdrawals and fresh water supplies to address water scarcity and significantly reduce Number of people who suffer from lack of water;

- by 2030, implement integrated water resources management at all levels, including through cross-border cooperation as appropriate;

- by 2020, protect and restore water-related ecosystems, including mountains, forests, wetlands, rivers, aquifers and lakes (UN-Water, 2016).

- by 2030, develop international cooperation and support to strengthen the capacity of developing countries in water and sanitation activities and programs, including the collection of waste water, desalination, rational use of water, wastewater treatment, recycling and reuse techniques;

- support and strengthen participation of local people in improving water and sanitation management (UN-Water, 2016).

This Sustainable Development Goal is a formal political commitment on the part of the international community to address the major water challenges, in particular the lack of access to water and sanitation, which still affects billions of people. Nowadays one in seven people on our planet, lack access to safe drinking water. More than 40 percent of the planet's population

will be living in areas of "severe" water stress and around 768 million people do not have access to a safe, reliable source therefore water pollution has become to a major global problem and it is leading worldwide cause of deaths and diseases.

2. Analysis of the recent researches and publications.

Pollution of the biosphere with toxic metals has accelerated dramatically since the beginning of the Industrial Revolution (Nriagu, 1979; Seifi-Nigje Gheshlagh et al., 2013; UN-Water, 2016; Ziarati et al., 2016). Wetland is a water environment which has considerable scientific, economic and social values. They are the habitats of various organisms contributing to the gene cache of microbes, plants and animals on the earth. However, nowadays the pollution and degradation of the wetlands are increasing dramatically (Dadgar et al., 2014). Marine animals can accumulate metals through sea water, suspended particles, sediments and food chains (Saghali et al., 2013). Permanent contaminants such as metals may be transferred to higher levels in the food chain through environmental expansion. Behavior of trace elements in various weathering environments is dramatically different. In world soil neutral or alkaline weathering environments, U, V, Mo, and Zn have high mobility, while Mn, Pb, Ba, Be, and Bi have low mobility, and Cu, Co, Fe, Ni, Th, Y have very low mobility. Otherwise in reducing environment conditions As, Ba, Be, Bi, Cd, Co, Cu, Mo, Ni, Pb, Se, Th, U, Zn, V, and Y have a very low degree of mobility (Abbaslou et al., 2014). Various technologies nowadays are used for the removal of heavy metals as evaporation, Ion exchange, precipitation, membrane filtration, and adsorption (Fenglian & Qi, 2011). Among all these technology adsorption process appears to be more favorable technology as it is low cost, require low maintenance, economical and is energy efficient.

Adsorption is a process where the atoms, ions or molecules of dissolved solids from liquid grips on the surface of solid; i.e. it is a process of mass transfer in which the dissolved solid from liquid gets deposited on the surface of solid because of physical or chemical interaction (Babel & Kurniawan, 2003). The major factors of this method are the technical applicability and the cost effectiveness that needs to be considering while selecting adsorbent to treat wastewater. Adsorbents are of different types and are classified as natural materials, industrial waste, agricultural and biological waste (Babel & Kurniawan, 2003; Siti Nur et al., 2013).

Adsorption has emerged out as effective, economical and ecofriendly treatment technique. It is a process potent enough to fulfill water reuse obligation and high effluent standards in the industries. Adsorption is basically a mass transfer process by which a substance is transferred from the liquid phase to the surface of a solid, and becomes bound by physical and/or chemical interactions (Babel & Kurniawan, 2003). It is a partition process in which few components of the liquid phase are relocated to the

surface of the solid adsorbents. All adsorption methods are reliant on solid-liquid equilibrium and on mass transfer rates. The adsorption procedure can be batch, semi-batch and continuous. At molecular level, adsorption is mainly due to attractive interfaces between a surface and the group being absorbed. The removal of heavy metals by using low cost adsorbent is found to be more encouraging in extended terms as there are several materials existing locally and profusely such as natural materials, agricultural wastes or industrial by-products which can be utilized as low-cost adsorbents (Siti Nur et al., 2013; Ahmadi et al., 2013; Yazdanparast et al., 2014; Razafsha & Ziarati, 2016; Motaghi & Ziarati, 2016; Ziarati et al., 2016; Pourzare et al., 2017). To be commercially viable, an adsorbent should have high selectivity to facilitate quick separations, favorable transport and kinetic characteristics, thermal and chemical stability, mechanical strength, resistance to fouling, regeneration capacity and low solubility in the liquid in contact. Adsorption process has several advantages over the conventional methods of heavy metal removal. Some of the gains of adsorption process are: (I) Economical, (II) metal selectivity, (III) Regenerative, (IV) Absence of toxic sludge generation (V) metal recovery and most importantly (VI) effective. Various low-cost adsorbent derived from various natural as well as anthropogenic sources have been implemented for treatment of waste water contaminated with heavy metals. The adsorbents mostly used are agricultural waste, industrial byproducts, natural materials or modified biopolymer (Yazdanparast et al., 2014; Razafsha & Ziarati, 2016; Motaghi & Ziarati, 2016; Ziarati et al., 2016; Pourzare et al., 2017).

Hibiscus sabdariffa L. commonly known as Roselle or red sorrel is a tropical plant which belongs to the family Malvaceae, widely grown in central and West Africa and South-East Asia. In the early 1970s Roselle has expected great considerable attention as a potential source of natural food colorant, pharmaceutical and cosmetics (Buasri et al., 2012). The thick, red and fleshy, cup shaped calyces of the Roselle flowers are consumed worldwide as food or a food ingredient such as jellies, syrups, beverages, puddings, cakes, wines and as a colorant. In addition to their use in food, various parts of the Roselle plant have been used in traditional medicine for the prevention of disease such as cardiovascular disease, liver disease, fever and hypertension. Previous studies have shown that Roselle can prevent cancer, lower blood pressure and improve the digestive system in humans. Its calyces extract has also been used as an effective treatment for patients with kidney stones (Pouget et al., 1990; Prenesti et al., 2007).

Sorrel, *H. sabdariffa* L. (Family Malvaceae), a medicinal herb commonly uses to make drink and pickle, is used in folk medicine in the treatment of hypertension, liver diseases, and fever (Pouget et al., 1990; Prenesti et al., 2007; Rodrigues & Pinto, 2007). *Hibiscus anthocyanins*, a group of phenolic natural pigment present in the dried flower of *H. sabdariffa* and *Hibiscus var. rosa sinensis*, have been found to have cardioprotective, hypocholesterolemic, antioxidative, and hepatoprotective effects in animals ((Pouget et al., 1990;

Shil et al., 2005; Prenești et al., 2007; Rodrigues & Pinto, 2007; Salazar-Gonzales et al., 2012). As Metal biosorption is the removal of metal ions by inactive, nonliving biomass due to highly attractive forces present between them. Particularly, it is due to the presence of certain functional groups, such as amine, carboxyl, hydroxyl, phosphate, sulfhydryl etc., on the cell wall of the biomass. In this study, the main goal is investigation on Bio-adsorption capacity of *Hibiscus sabdariffa* L. commonly known as Roselle or red sorrel in a batch system by considering the effects of various parameters like initial concentration, pH, contact time, temperature, agitation speed and bio-adsorbent dose. The other factor that in current study is very important is the accompanying of black tea residue by red tea in order to increase effect of bio-adsorption effect in removal of Cadmium, Cobalt and Nickel from contaminated waste water (Razafsha & Ziarati, 2016; Motaghi & Ziarati, 2016; Ziarati et al., 2016; Pourzare et al., 2017).

3. Statement of the problem and its solution.

3.1. Materials and method.

The flower and sepal of *H. sabdariffa* L. (figure 1) by local name of red tea were purchased from Fenoj region in Sistan province in the south-eastern region of Iran (figure 2).



Figure 1 – *Hibiscus sabdariffa* L.



Figure 2 – Location of *H. sabdariffa* L. samples collection in the south-eastern region of Iran

Samples were transferred into glass container and preserved until extraction procedure was performed in the laboratory in May 2017 in order to investigate the influence of its residue in addition of black tea residue as low-cost adsorbents for removal of heavy metals. Due to investigation on their potential of removing heavy metals from contaminated waste waters, Dehydrated Roselle sepals after 10 minutes infusion by 70 °C, then dried at 30±2 °C using solar drying, mix by black tea residue after infusion in 10 minutes by different percentage.

The initial concentration of heavy metals/metalloid such as Nickel, Cobalt and Lead in the untreated waste waters and also treated by *H. sabdariffa* L. sepal residue in addition of black tea residue as were analyzed. After especial times: 1, 5, 10, 15, 30, 40 minutes (by stirring) final concentration of heavy metals in effluent samples were analyzed using Atomic Absorption Spectroscopy. The samples were analyzed by an Atomic Absorption Spectrophotometer Model AA-6200 (Shimadzu, Japan) using an air-acetylene flame for heavy metals and using at least five standard solutions for each metal. All required precautions were taken to avoid any possible contamination of the sample as per the AOAC guidelines (AOAC, 2000; Ziarati & Rabizadeh, 2013; Ziarati & Azizi, 2013; ORA Laboratory Manual FDA, 2013). The efficiency of *H. sabdariffa* L. sepal residue in accumulating heavy metals was investigated.

3.2. Statistical Analysis.

The values reported here are means of five values. Data were tested at different significant levels using student t-test to measure the variations between the contaminations in wastewater and the dose of bio-adsorbent and contact time parameters before and after treated by *R. crispus* seeds. One way analysis of variance (ANOVA) was used for data analysis to measure the variations of metal concentrations using SPSS 22.0 software (SPSS Inc, IBM, Chicago, IL).

4. Results.

The mean content of heavy and mineral elements: Cadmium, Cobalt and Nickel in presence of red tea (*H. sabdariffa* L. sepal) residue samples collected from Sistan Province in the south of Iran after 10 minutes infusion in accompany of black tea residue are shown in table 1 and figures 3–5. The samples were analyzed by wet digestion method and standardized international protocols were followed for the preparation of material and analysis of heavy metals contents and analyzed by Atomic Absorption Spectrophotometer in Research Laboratory in Pharmaceutical Sciences Branch, Islamic Azad University. The data obtained from chemical analyses, mean values were calculated and are given in the table 1.

Figure 3 shows the bio-adsorption of cadmium by residue of red tea (*H. sabdariffa* L.) sepal samples after 10 minutes infusion in accompany by black tea residue in different concentrations during a functional factor of time. Initial Cadmium concentration 50.032 mg/l and bio-adsorbents dose of 0.1, 0.2, 0.3 and 0.5 mg/100ml of residue of red tea in addition of black tea waste materials after infusion in 10 minutes were used and the study followed in 6 specified time: 1, 5, 10, 15, 30 and 40 minutes. Figure 3 indicates that rapid adsorption in the initial 40 minutes for all bio-adsorbent. Mostly, the removal of cadmium is rapid, but it gradually decreases with time until it reaches equilibrium. The necessary time to reach this equilibrium is about 40 minutes. Further increase in contact time more than 40 minutes did not show significant increase in bio-adsorption ($p > 0.05$). The best results obtained by 0.5 % of red tea + 3 % black tea residues.

Table 1 – Mean value ±SD of Cadmium, Cobalt and Nickel contents (mg /L) after addition of different percentages of *H. sabdariffa* L. sepal and black tea residue

Mean Cd content (mg/L)	Time of contact					
	1 min	5 min	10 min	15 min	30 min	40 min
0.1 % bio-adsorbent <i>H. sabdariffa</i> L. sepal + 1 % black tea residue	48.54 ^a	45.312 ^b	35.785 ^c	33.552 ^c	31.102 ^c	28.779 ^d
0.2 % bio-adsorbent <i>H. sabdariffa</i> L. sepal + 2 % black tea residue	48.04 ^a	42.338 ^b	33.217 ^c	32.574 ^c	32.111 ^c	26.788 ^d
0.3 % bio-adsorbent <i>H. sabdariffa</i> L. sepal + 3 % black tea residue	47.03 ^a	38.195 ^b	32.067 ^c	28.974 ^c	26.571 ^c	17.454 ^d
<u>0.5 % bio-adsorbent <i>H. sabdariffa</i> L. sepal + 3 % black tea residue</u>	44.12 ^a	34.187 ^b	30.107 ^c	27.651 ^c	14.092 ^d	8.732 ^d
untreated contaminated Effluent	50.032 ^a	50.021 ^a	49.868 ^a	49.866 ^a	49.964 ^a	49.866 ^a
Mean Co content (mg/L)	1 min	5 min	10 min	15 min	30 min	40 min
0.1 % bio-adsorbent <i>H. sabdariffa</i> L. sepal + 1 % black tea residue	103.42 ^a	97.106 ^a	95.602 ^a	93.116 ^a	93.217 ^a	91.181 ^b
0.2 % bio-adsorbent <i>H. sabdariffa</i> L. sepal + 2 % black tea residue	100.88 ^a	98.419 ^a	94.333 ^a	91.018 ^b	89.806 ^b	88.112 ^b
0.3 % bio-adsorbent <i>H. sabdariffa</i> L. sepal + 3 % black tea residue	100.01 ^a	90.154 ^b	89.094 ^b	86.731 ^b	80.556 ^c	78.667 ^c
<u>0.5 % bio-adsorbent <i>H. sabdariffa</i> L. sepal + 3 % black tea residue</u>	98.65 ^a	87.28 ^b	86.564 ^b	83.211 ^b	78.444 ^c	70.193 ^c
untreated contaminated Effluent	110.21 ^a	110.45 ^a	109.89 ^a	109.88 ^a	110.23 ^a	110.35 ^a
Mean Ni content (mg/L)	1 min	5 min	10 min	15 min	30 min	40 min
0.1 % bio-adsorbent <i>H. sabdariffa</i> L. sepal + 1 % black tea residue	106.52 ^a	100.03 ^a	95.556 ^b	93.213 ^b	90.617 ^b	82.187 ^c
0.2 % bio-adsorbent <i>H. sabdariffa</i> L. sepal + 2 % black tea residue	102.89 ^a	97.632 ^a	92.206 ^b	90.111 ^b	85.345 ^c	78.432 ^d
0.3 % bio-adsorbent <i>H. sabdariffa</i> L. sepal + 3 % black tea residue	95.498 ^a	91.222 ^b	89.704 ^b	84.532 ^c	80.556 ^c	76.562 ^d
<u>0.5 % bio-adsorbent <i>H. sabdariffa</i> L. sepal + 3 % black tea residue</u>	90.478 ^b	80.778 ^c	74.306 ^d	68.092 ^d	60.232 ^d	50.32 ^f
untreated contaminated Effluent	110.15 ^a	111.9 ^a	110.16 ^a	110.87 ^a	110.34 ^a	110.28 ^a

**Small letter in a row, showed significant differences with each other (p < 0.05).

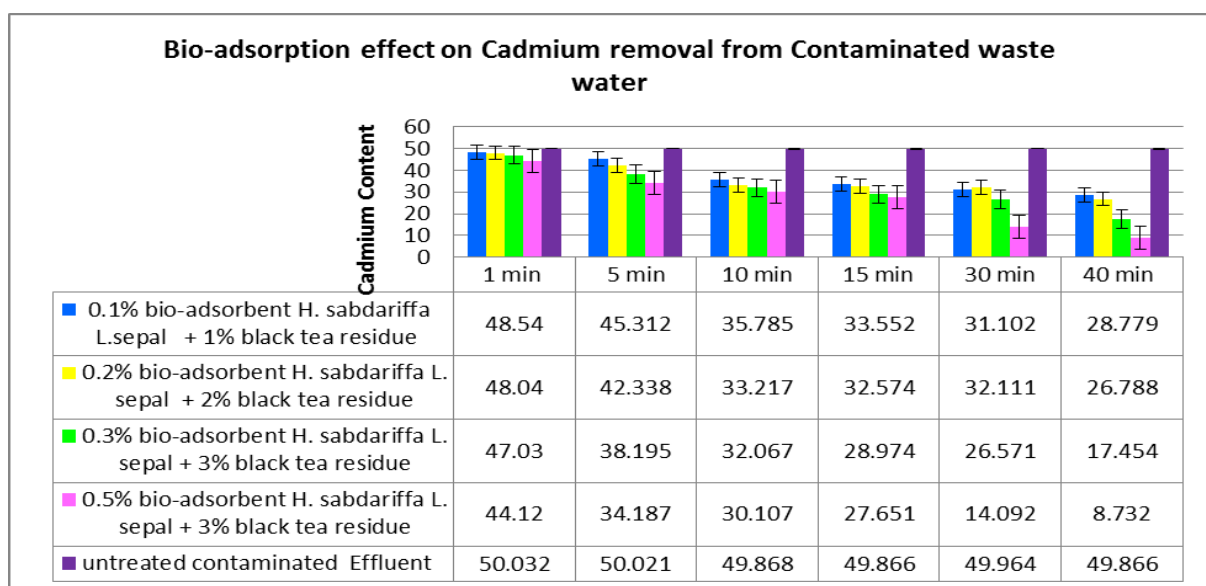


Figure 3 – Effect of contact time on the removal of cadmium (initial Zinc concentration = 50.032 mg/l, adsorbent dose of red tea residue = 0.1, 0.2, 0.3 and 0.5 mg/100 ml in accompany of black tea residue, temperature = 25 ± 1 °C, agitation speed = 400 rpm, pH = 3.5, and the study followed in 6 specified time: 1, 5, 10, 15, 30 and 40 minutes

Figure 4 shows the bio-adsorption of cobalt by residue of red tea (*H. sabdariffa* L.) sepal samples after 10 minutes infusion in accompany by black tea residue in different concentrations during a functional factor of time. Initial Cadmium concentration 110.21 mg/l and bio-adsorbents dose of 0.1, 0.2, 0.3 and 0.5 mg/100ml of residue of red tea in addition of black tea waste materials after infusion in 10 minutes were used. Figure 4 indicates that rapid adsorption was not happening and the potential of bio-adsorbents for

removing cobalt is not the same as cadmium trend. Mostly, the removal of cadmium is rapid, but it decreasing of cobalt happened by lower kinetic and gradually decreases with time until it reaches equilibrium. The necessary time to reach this equilibrium is the same as cadmium and it is about 40 min. Further increase in contact time more than 40 minutes did not show significant increase in bio-adsorption ($p > 0.05$). The best results obtained by used 0.5 % of red tea + 3 % black tea residues.

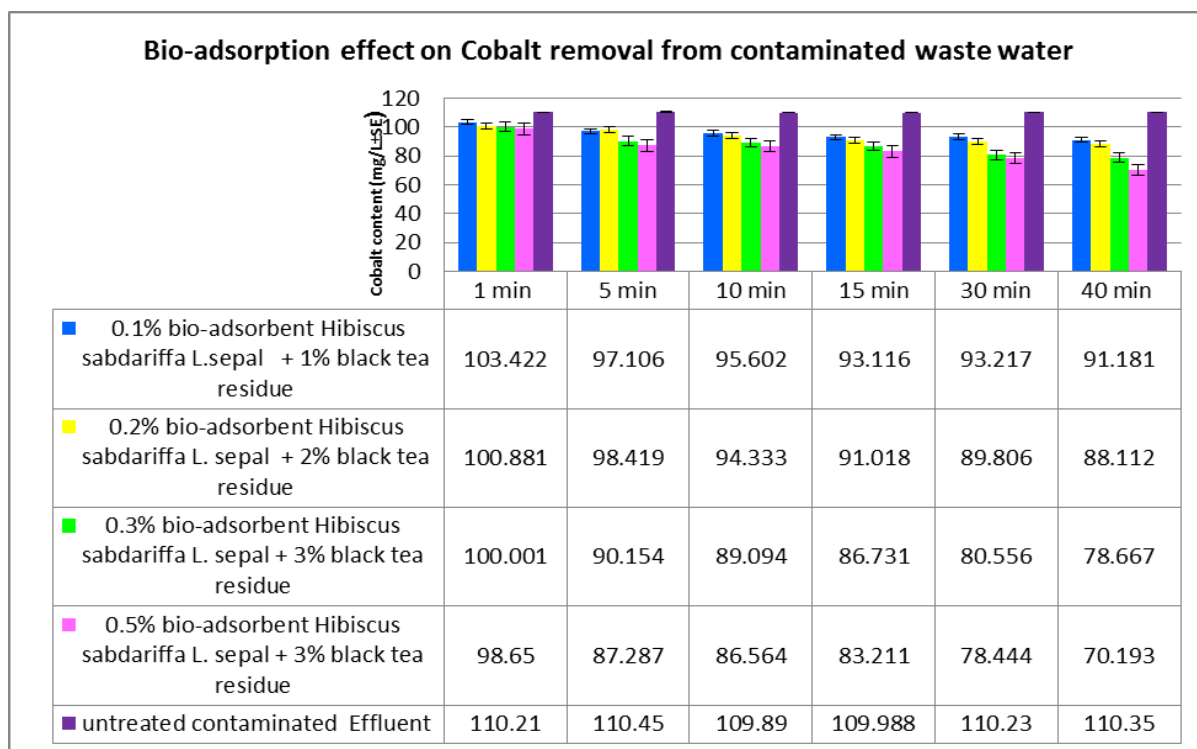


Figure 4 – Effect of contact time on the removal of cobalt (initial Cobalt concentration = 110.21 mg/l, adsorbent dose of red tea residue = 0.1, 0.2, 0.3 and 0.5 mg/100 ml in accompany of black tea residue, temperature = 25 ± 1°C, agitation speed = 400 rpm), pH = 3.5

Figure 5 shows the bio-adsorption of Nickel by residue of red tea (*H. sabdariffa* L.) sepal samples after 10 minutes infusion in accompany by black tea residue in different concentrations during a functional factor of time. Initial Nickel concentration 110.15 mg/l and bio-adsorbents dose of 0.1, 0.2, 0.3 and 0.5 mg/100ml of residue of red tea in addition of black tea waste materials after infusion in 10 minutes were used. Figure 5 indicates that rapid adsorption happening was after 10 minutes for 0.5 % red tea + 3 % black tea residue and the potential of bio-adsorbents for removing Nickel is the same as cadmium trend. Mostly, the removal of Nickel by 0.5 % red tea and 3 % black tea residue is so rapid and after 40 minutes approximately 50 % of Nickel contents were adsorbed and the adsorbing rate was significantly increased by the factor of time and concentration of adsorbents. The necessary time to reach this equilibrium is about 15 minutes. Further increase in contact time more than 40 minutes similar to other studied heavy metals in this study did not show significant increase in bio-

adsorption ($p > 0.05$). The best results obtained by 0.5 % of red tea + 3 % black tea residues.

5. Discussion.

Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a molecular or atomic film (the adsorbate). Adsorption is operative in most natural physical, biological, and chemical systems, and is widely used in industrial applications such as activated charcoal, synthetic resins and water purification. Among these methods, adsorption is currently considered to be very suitable for wastewater treatment because of its simplicity and cost (Yadanaparthi et al., 2009; Kwon et al., 2010). Adsorption is commonly used technique for the removal of metal ions from various industrial effluents (Ramakrishna & Susmita, 2012). Activated carbon is the most widely used adsorbent. It is a highly porous, amorphous solid consisting of micro crystallites with a graphite lattice, usually prepared in small pellets or a powder.

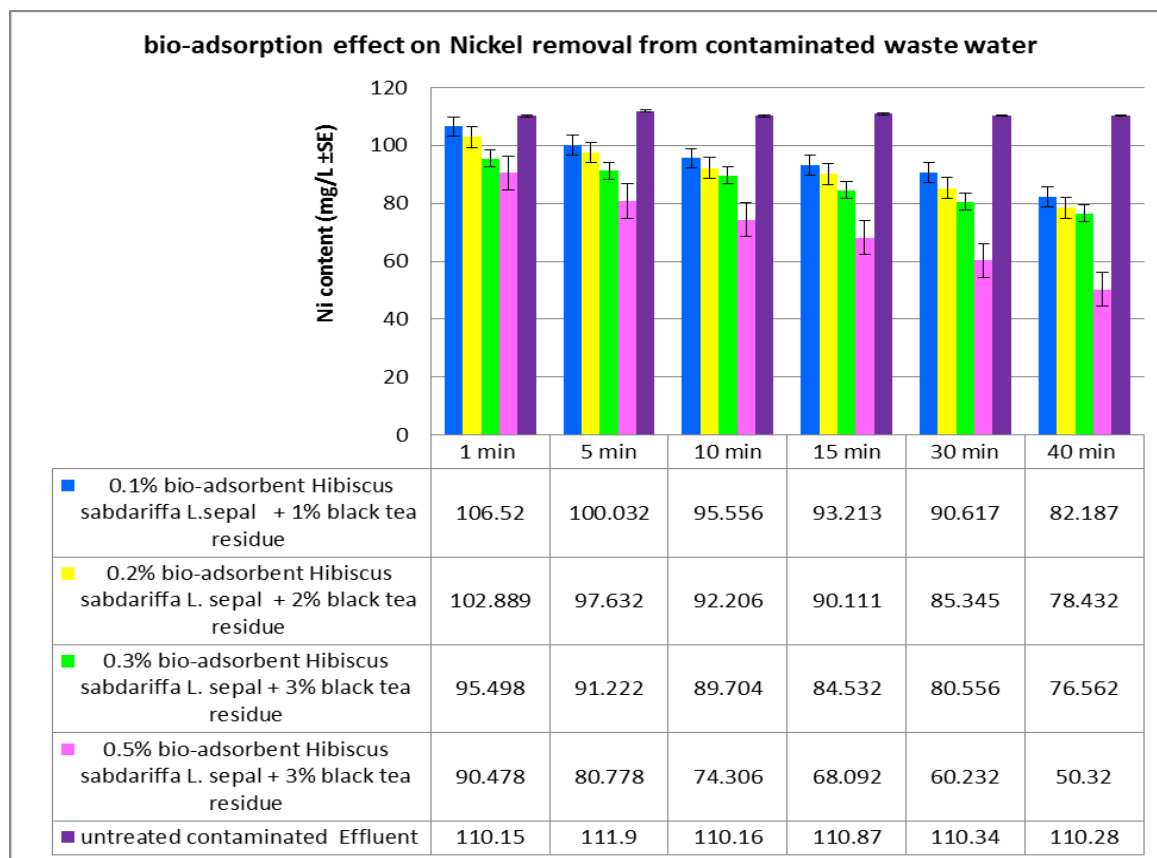


Figure 5 – Effect of contact time on the removal of nickel (initial Ni concentration = 110.15 mg/l, adsorbent dose of red tea residue = 0.1, 0.2, 0.3 and 0.5 mg/100 ml in accompany of black tea residue, temperature = 25 ± 1 °C, agitation speed = 400 rpm), pH = 3.5

It can remove a wide variety of toxic metals. Some widely used adsorbents for adsorption of metal ions include activated carbon (Satapathy & Natarajan, 2006), clay minerals (Wang et al., 2008), biomaterials, industrial solid wastes and zeolites (Sinha et al., 2004). Natural material or certain waste from industrial or agricultural operation is one of the resources for low cost adsorbents.

Contaminant uptake by plants and its mechanisms have been being explored by several researchers. It could be used to optimize the factors to improve the performance of plant uptake. According to Sinha et al. (2004), the plants act both as «accumulators» and «excluders». Accumulators survive despite concentrating contaminants in their aerial tissues. They biodegrade or bio transform the contaminants into inert forms in their tissues. The excluders restrict contaminant uptake into their biomass. Plants have evolved highly specific and very efficient mechanisms to obtain essential micronutrients from the environment, even when present at low ppm levels. Plant roots, aided by plant-produced chelating agents and plant induced pH changes and redox reactions, are able to solubilize and take up micronutrients from very low levels in the soil, even from nearly insoluble precipitates. Plants have also evolved highly specific mechanisms to translocate and store micronutrients.

These same mechanisms are also involved in the uptake, translocation, and storage of toxic elements, whose chemical properties simulate those of essential elements. Thus, micronutrient uptake mechanisms are of great interest to phytoremediation (Srivastava et al., 2005; Subhashini & Swamy, 2013). The range of known transport mechanisms or specialized proteins embedded in the plant cell plasma membrane involved in ion uptake and translocation include (1) proton pumps (-ATPases that consume energy and generate electrochemical gradients), (2) co- and anti-transporters (proteins that use the electrochemical gradients generated by -ATPases to drive the active uptake of ions), and (3) channels (proteins that facilitate the transport of ions into the cell). Each transport mechanism is likely to take up a range of ions. A basic problem is the interaction of ionic species during uptake of various heavy metal contaminants. After uptake by roots, translocation into shoots is desirable because the harvest of root biomass is generally not feasible. Little is known regarding the forms in which metal ions are transported from the roots to the shoots (Brady et al., 1994). Plant uptake-translocation mechanisms are likely to be closely regulated. Plants generally do not accumulate trace elements beyond near-term metabolic needs (Brady et al., 1994).

For adsorption from solution with the additional assumption that layers beyond the first have equal

energies of adsorption, the Brunauer-Emmett-Teller equation takes the simplified form.

The adsorbent used in the experimental work is a commercially available, and they are the waste of tea that could be collected in every house with no cost in fact (Brady et al., 1994). Contact Time

Bio-sorption of heavy metals can increase with increasing contact time (figures 3, 4 and 5, and table 1). This could be attributed to the transfer of higher amount of bio-sorbent from solution phase to the bio-sorbent active sites as contact time increases.

Another reason for increased sorption of heavy metals with protracts stirring time could be due to the reduced bound covering resistance to the transfer of biomass in solution and enhanced heavy metals kinetic energy (Brierley et al., 1993; Krauter et al., 1996).

The results of current study revealed that heavy metals adsorption ranged from 31...50 % after agitation for 40 minutes (equilibration time), and there was no significant further increase in % sorption of them after the equilibration time ($p \geq 0.05$).

Bio-adsorbent Dose

Bio-adsorbent dose is one of the most important factors which affect significantly on influence specific uptake of all studied heavy metals: Nickel, Cadmium and Cobalt from waste water effluent. Generally, for low bio-adsorbent dose, there is an enhanced heavy metals sorption especially for Cd and Sorption capacity of different bio-adsorbents have been observed to reduce with increasing bio-adsorbent dose (table 2, figure 3 and 5).

A potential bio-adsorbent for Cobalt removal must be selected on the basis of its high sorption capacity, so that the bio-adsorbent could be reconstructed and rephrased. Bio-adsorbents from agricultural waste and also herbal tea residue or food industry are considered to be cost-effective and easily available; therefore, post-bio-adsorption disposal of Cd-loaded biomass at landfill sites could be another option. The current research indicated that this could reduce the volume of total biomass and release heavy metals mainly as safe form (Brady et al., 1994 ; Subhashini & Swamy, 2013).

Metal biosorption is the removal of metal ions by inactive, nonliving biomass due to highly attractive forces present between the two (Salman et al., 2014). Particularly, it is due to the presence of certain functional groups, such as amine, carboxyl, hydroxyl, phosphate, sulfhydryl etc., on the cell wall of the biomass (Yoon et al., 2006). The process involves a solid phase (biomass) and a liquid phase containing metal ions (solution of metal ions/waste-water). Metal ions are attracted and bound to the biomass by a complex process that comprises of a number of mechanisms like adsorption on the surface and pores, ion-exchange, surface precipitation, complexation and chelation and entrapment in capillaries and spaces of polysaccharide network, due to the concentration causing diffusion through the cell wall and membrane. To study the mechanism, it is necessary to have the exact information about the cell wall structure of the

biomass as well as the solution chemistry (Puranik et al., 2005).

Factors Affecting the Bio-adsorption

The investigation of the efficacy of the metal uptake by the microbial biomass is essential for the industrial application of bio-adsorption, as it gives information about the equilibrium of the process which is necessary for the design of the equipment. The following factors affect the bio-adsorption process:

1. Temperature seems not to influence the bio-adsorption performances in the range of 20...35 °C (Brady et al., 1994; Subhashini & Swamy, 2013).

2. pH seems to be the most important parameter in the bio-adsorptive process: it affects the solution chemistry of the metals, the activity of the functional groups in the biomass and the competition of metallic ions (Brady et al., 1994; Srivastava et al., 2005; Subhashini & Swamy, 2013; Salman et al., 2014).

3. Biomass concentration in solution seems to influence the specific uptake: for lower values of biomass concentrations there is an increase in the specific uptake.

4. Bio-adsorption is mainly used to treat wastewater where more than one type of metal ions would be present; the removal of one metal ion may be influenced by the presence of other metal ions. According to the location where the metal removed from solution is found, bio-adsorption can be classified as: (a) Extra cellular accumulation/ precipitation, (b) Cell surface sorption/ precipitation, (c) Intracellular accumulation (Srivastava et al., 2005; Puranik et al., 2005; Subhashini & Swamy, 2013; Salman et al., 2014).

Conclusions.

In current study, we considered the sources and toxicology of heavy metals as well as the reason why they need to be removed from our environment. The results of current study revealed that using 0.5 % red tea residue in accompany by 3 % black tea residue can remove and decrease Cadmium and Nickel significantly and for Cobalt decreasing the rate of adsorption is not as much as 2 other metals but remove Cobalt after 40 minutes in remarkable contents. Conventional methods of removal are mostly expensive or take too many times. Therefore, the uses of low-cost, abundant environmentally friendly bio-adsorbents have been surveyed and investigated. Most studies in the bio-adsorption field have been and are still being conducted to pinpoint the best bio-adsorbent and alternative adsorbents with high adsorption capacity although bio-adsorption is promising; its mechanism is not well elucidated. The advanced development of the bio-adsorption processes requires further improvement in the direction of modeling, regeneration of bio-adsorbent material and of testing immobilized raw biomasses with basic industrial effluents. As the waste and residue of black tea and red tea are abundant and cheap and the high synergic adsorption capacity of them are confirmed in current study, authors recommend to utilized them and recommend to study on the other waste materials due to find the best and optimum situation for cleaning up waste waters.

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Conflicts of Interest

None of the authors have any conflicts of interest associated with this study.

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БІО-АДСОРБЦІЯ ВАЖКИХ МЕТАЛІВ ІЗ ЗАБРУДНЕНОЇ ВОДИ З ВИКОРИСТАННЯМ *HIBISCUS SABDARIFFA L.*

Біoadсорбція металу – це видалення іонів металів неактивною, неживої біомасою. Вивчено біoadсорбційна здатність *Hibiscus sabdariffa L.*, широко відомого як Roselle або червоний шавель, з регіону Feroo провинції Sistan в південно-східній частині Ірану, для очищення стічних вод при зміні початкової концентрації, рН, часу контакту, температури, швидкості перемішування й дози біoadсорбента. Відповідно до підвищення біoadсорбційної здатності залишки чорного чаю додавали до залишків червоного чаю в різних концентраціях. Змінюючи значення рН і температури, було вивчено співвідношення залишків червоного і чорного чаю при впливі на забруднений розчин стічних вод при різному часі контакту, початковій концентрації, розмірі частинок й швидкості перемішування. Зразки були проаналізовані стандартизованими міжнародними протоколами в Дослідницькому центрі з питань харчування і харчових наук у Відділі фармацевтичних наук Ісламського університету Азад. Кращі результати, отримані на 0,5 % червоного чаю + 3 % залишків чорного чаю через 40 хвилин. Подальше збільшення часу контакту більше 40 хвилин не показало значного збільшення біoadсорбції ($p > 0,05$). Результати цього дослідження показали, що використання 0,5 % залишків червоного чаю в суміші з 3 % статки чорного чаю може значно вилучати кадмій і нікель із забрудненої води. Для кобальту, швидкість адсорбції трохи нижче, ніж для перших двох металів, але впродовж 40 хвилин він також адсорбується із забрудненої води.

Ключові слова: біoadсорбція; червоний чай; чорний чай; важкі метали; забруднена вода.

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БИО-АДСОРБЦИЯ ТЯЖЕЛЫХ МЕТАЛЛОВ ИЗ ЗАГРЯЗНЕННОЙ ВОДЫ С ПРИМЕНЕНИЕМ *HIBISCUS SABDARIFFA* L.

Биоадсорбция металла – это удаление ионов металлов неактивной, неживой биомассой. Изучена биоадсорбционная способность *Hibiscus sabdariffa* L., широко известного как Roselle или красный щавель, из региона Feroz провинции Sistan в юго-восточной части Ирана, для очистки сточных вод при изменении начальной концентрации, pH, времени контакта, температуры, скорости перемешивания и дозы биоадсорбента. В соответствии с повышением биоадсорбционной способности остатки черного чая добавляли к остаткам красного чая в разных концентрациях. Изменяя значения pH и температуры, было изучено соотношение остатков красного и черного чая при воздействии на загрязненный раствор сточных вод при различном времени контакта, начальной концентрации, размере частиц и скорости перемешивания. Образцы были проанализированы стандартизованными международными протоколами в Исследовательском центре по вопросам питания и пищевых наук в Отделе фармацевтических наук Исламского университета Азад. Лучшие результаты, полученные на 0,5 % красного чая + 3 % остатков черного чая через 40 минут. Дальнейшее увеличение времени контакта более 40 минут не показало значительного увеличения биоадсорбции ($p > 0,05$). Результаты текущего исследования показали, что использование 0,5 % остатков красного чая в смеси с 3 % остатков черного чая может значительно извлекать кадмий и никель из загрязненной воды. Для кобальта, скорость адсорбции несколько ниже, чем для первых двух металлов, но в течении 40 минут он также адсорбируется из загрязненной воды.

Ключевые слова: биоадсорбция; красный чай; черный чай; тяжелые металлы; загрязненная вода.