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# NOVEL METHOD IN REMOVING NICKEL AND COBALT FROM PHARMACEUTICAL LABORATORIES' EFFLUENT BY GREEN BIO-ADSORBENT: TOMATO POMACE

**Maryam Mokhtarzadeh[1], Parisa Ziarati[2*], Javad Hosseini[1]**

[1]Department of Applied Chemistry, Faculty of Pharmaceutical Chemistry, Tehran Medical Sciences, Islamic Azad University, Tehran, Iran
[2]Department of Medicinal Chemistry, Faculty of Pharmacy and Pharmaceutical Sciences, Tehran Medical Sciences, Islamic Azad University, Tehran, Iran

**Abstract.** The sustainable removal of toxic heavy metals from Pharmaceutical effluent has become one of the major concerns and challenges to scientists and engineers, despite there are numerous treatment technologies. The Bio-adsorption technique for removing Cobalt and Nickel ions ($M^{+2}$) by Tomato Pomace Waste (TPW) as an environmentally residue which can be spoiled itself and should be treated, investigated. Tomato pomace is one of the by-products of the tomato paste industry and in current study Tomato pulp, pomace and seeds residue were collected from recognized Tomato paste Industries in Tehran county in August and September 2020. The 920 treated wastewater samples by TPW, have been analyzed for two weeks and the heavy metal contents: Nickel and Cobalt in each studied sample analyzing by wet digestion method and determined by ICP-MS. Data Analysis of variance revealed that after 48 hours in the presence of tomato biomass adsorbent, the concentration of Cobalt and Nickel decreased significantly and current green study showed, %63.93 of Nickel and %69.98 of Cobalt can easily remove from Pharmaceutical contaminated effluent.

***Keywords:*** *Heavy metals, tomato pomace, pharmaceutical effluent, adsorption, detoxification.*

****Corresponding Author:*** *Parisa Ziarati, Faculty of Pharmacy and Pharmaceutical Sciences, Tehran Medical Sciences, Islamic Azad University, No 99, Yakhchal, Gholhak, Dr. Shariati, Tehran, Iran, Tel:+98-21-22640051; Fax: +98-21-22633986, e-mail: ziarati.p@iaups.ac.ir parziarati@gmail.com*

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## 1. Introduction

Nowadays, water pollution by heavy metals has become a major concern for human health that developing and industrialized countries face. The accumulation of these metals in animals and plants, in addition to serious damage to the health of these organisms, has made the consumption of their products dangerous for the final consumer, namely humans. Almost all heavy metals in the body have adverse effects (Shirkhan, *et al.*, 2022; Tajik *et al.*, 2020; Fatahi *et al.*, 2020; Jalillian & Ziarati, 2016).

These include disorders of the nervous, renal and circulatory systems. Water pollution is divided into three categories, which include industrial, urban and agricultural pollution. Urban water pollution actually includes effluents from homes and businesses. So far, the main purpose of research on such effluents has been to reduce particulate matter, hard materials, solubility of inorganic compounds, and so on (Plazzotta *et al*., 2017; Yazdanparast *et al.*, 2014; Ziarati *et al*., 2016a).

Heavy metals are among their health problems due to the serious and dangerous complications and problems they have always had for the environment and humans (Ziarati *et al*., 2015a).

Currently, the removal of heavy metals from municipal and industrial wastewaters is one of the most important events that should be done as best as possible because heavy metals are biodegradable and their bioaccumulations are very dangerous. Contaminated effluents should be removed before discharge, as contact with these metals can have very unpleasant consequences, such as neurological disorders, cellular aging, liver and kidney failure, and so on (Saratale *et al*., 2008; Sabiiti, 2011; Alimardan *et al.,* 2016).

Heavy metals as a hazardous problem of various dimensions can seriously endanger human life and other living organisms and cause acute and chronic poisoning. Heavy metals have the ability to accumulate and their amount does not decrease and remain in the soil for thousands of years (Venkata Subhash & Venkata Mohan, 2014; Shokri *et al.,* 2016; Meharad *et al.,* 2016; Ziarati *et al.,* 2020a; Ziarati *et al.,* 2020b).

After entering the body, heavy metals are no longer excreted from the body, but accumulate and accumulate in tissues such as fat, bone, joints, muscles, and eventually cause diseases such as neurological disorders, various types of cancer, abortion, damage to Liver, kidneys and brain, arthritis, hair loss, respiratory disorders and osteoporosis occur in the human body (Ziarati *et al.,* 2020c).

Therefore, contamination of this product can endanger human health. Heavy metals such as Nickel, lead and mercury are dangerous toxins around us. These metals enter the natural cycle through water, soil and air through various natural and artificial sources and cause dangerous effects. Therefore, they are considered as a serious danger to the survival of living beings (Garadaghli, 2021; Ziarati *et al.,* 2019; Arancon *et al.,* 2013).

Studies have shown that fruit wastes are very effective in absorbing heavy metals due to their high ability to absorb and also due to their cellulosic, carbon and silica compounds. Biological wastes are both abundant and available and have no specific use. Since the late 32's, the use of natural bio-sorbents such as raw plant residues has evolved and the method of chemical modification (using fruit waste) has replaced the method of physical activation (activated carbon) which has advantages such as higher adsorption capacity and equilibrium time. Activation costs are much lower (Fatahi *et al.,* 2020; Tajik *et al.,* 2020).

The main aim of the study is to adsorb toxic and heavy metals by cheap and available tomato pomace waste as environmentally residue which obtained from the paste of manufacturing plants (Tomato paste factory ), in order to reduce the hazardous heavy metals Nickel and Cobalt from the effluent of pharmaceutical laboratories (MirMaohammad-Makki and Ziarati, 2015; Ziarati *et al.*, 2020d; Ziarati *et al.*, 2020e; Ziarati & MirMohammad-Makki, 2015).

Tomato with the scientific name of *Solanum lycopersicum* is one of the red vegetables or fruits (Heuzé *et al.,* 2015; Ziarati & Makki, 2014; Caluya *et al.,* 2003). This plant is native to South and Central America and was transferred to other parts of the world during the Spanish colonial period. Different types of this plant are grown all over the world today. Of course, tomato is considered in terms of horticulture and lack of kernels in the category of vegetables. Fresh tomato by-products have been considered an environmental nuisance for a long time (Del Valle *et al*., 2006). In some countries, the waste is dumped in water bodies near the factory or left to accumulate on the site of production. The material spoils quickly, emits a very foul odor and provides a breeding place for a variety of pests such as flies and mosquitoes, which are hosts of disease-causing organisms (León-García *et al.,* 2017). Feeding animals with tomato by-products is, therefore, a valuable way to prevent environmental contamination (Akilu *et al.,* 2020).

Due to its economic importance, this plant is the subject of many researches and is known in genetics as one of the model plants. Research on this plant in 1990 led to the production of the first transgenic species permitted for consumption and trade in the United States (Banerjee *et al.*, 2017).

Tomato pomace is one of the by-products of the tomato paste industry, which, depending on the processing method and characteristics of raw tomatoes, includes different proportions of skin, seeds and small amounts of tomato meat. Tomato pulp is one of the by-products that is obtained during the production process of tomato sauce and puree (Ehsani *et al.,* 2021).

Using sorbents to remove contaminants is one of the most promising methods. Tomato pulp is a plant residue and in this study, its adsorption capacity for selected contaminants in water has been investigated (Ziarati *et al.*, 2021f).

In order to achieve efficient, effective and especially cheap adsorbents, the path of studies of adsorption of heavy metals to natural materials (such as some waste products from industrial and agricultural operations) has changed, which is known as biomass (Ziarati *et al.*, 2021f).

The term wood biomass, short cycle wood products, agricultural wastes, short cycle plant species, wood wastes, industrial wastes, waste paper, sawdust, bio-soils, grass, food processing wastes, aquatic plants, wastes It contains algae and other groups of substances. In fact, biomass is a simple term for all organic matter of biological origin (Seifollahi *et al.*, 2017; Arabian *et al*., 2020; Ziarati *et al.*, 2020g).

Bio-sorbents have the property of removing metal from solutions and can also be used to reduce concentration (Shirkhan, *et al.,* 2022; Tajik *et al.,* 2020; Fatahi *et al.,* 2020). They can effectively separate ppb to ppm of heavy metal ions from the surface of dissolved metal ions from complex dilute solutions with high efficiency and speed. Therefore, bio-sorbents are an ideal candidate for the treatment of wastewater with a large volume and low concentration of heavy metals. Some of the advantages of bio-sorption over conventional treatment methods include low cost, high efficiency for solutions with low concentrations of heavy metals, minimal amount of chemical or biological sludge, no need for nutrients and the possibility of reactivation of the adsorbent and metal recovery (Ziarati & Tosifi, 2014; Mousavi *et al.,* 2014; Ziarati 2012).

The idea of utilizing Agro/Food waste as natural and available adsorbents due to removing heavy metals from contaminated soils and wastewater is not new. Many studies are conducted in this approach have been done recent years (Jafari *et al.,* 2016; Zahirnejad *et al.,* 2017; Shahsavan-Davoudi& Ziarati, 2020).

In 2020, Shahsavan and Ziarati studied the adsorption properties of grapefruit peels for removal the Arsenic, Cobalt, Lead, Cadmium and Chromium from Pharmaceutical effluent in Pharmaceutical Sciences faculty Tehran medical Sciences in Azad University in such a way that with increasing the size of bio-sorbent particles, absorption decreases and with decreasing the initial pH, time of contact of the solution by adsorbents and temperature the percentage of toxic metals significantly increased. Bio-sorbents treated with 1% tartaric acid at maximum capacity removed 10.01 mg/l of cadmium in the effluent and quickly removed it from the aqueous solution. Thermodynamic studies showed that the adsorption of cadmium on Grapefruit-biosorbent is a spontaneous and exothermic process and the results revealed that grapefruit peel can be considered as an effective adsorbent ( Makki and Ziarati 2015; Ziarati & Mirmohammad-Makki, 2015; Shahsavan-Davoudi & Ziarati, 2020; Alimardan *et al.*, 2016). Tavakoli and Ziarati (2018) investigated removal yields of Lead, Nickel and Cadmium contents of edible vegetables using Apricot Shell. Thus, detoxification of heavy metals in plants, a serious issue before being used for food processing and human consumption, finds a better treatment process with Apricot. Heavy metal related illnesses and chronic degenerative conditions can be avoided in various plants Parsley (*Petroselinum crispum*); holy basil (*Ocimum tenuiflorum*); *Coriandrum sativum*; and Cress (*Lepidium sativum*); using Apricot Shell treatment in Soil. The removal of heavy metals from the contaminated agricultural soil, in Yazd city, had done by apricot kernel hard shell. Different adsorption parameters such as adsorbent dose, adsorbent particle size and plant growth time were examined, composite soil samples were collected from four agricultural areas of Yazd city, leafy vegetables under similar controlled physical conditions including pH, light, irrigation and humidity. The apricot kernel had the ability to adsorb significantly heavy metals from the contaminated soil along with leafy vegetables were cultivated by different contents of bio-adsorbent (Tavakoli-Hosseinabady *et al.*, 2018).

In 2018-2021, Ziarati et al. reviewed the analysis of methods for the removal of toxic heavy metals by bio-sorbents. The main purpose of this article is to evaluate the potential, reliability and effectiveness of using agricultural waste and agricultural waste to significantly eliminate or reduce Heavy metals are contaminated with food and water (Ziarati *et al.*, 2020a).

The main aim of the study was to adsorb toxic and heavy metals by cheap and available tomato pomace waste as environmentally residue that can be spoiled quickly. It is considered as an environmental nuisance itself from the paste of manufacturing plants (Tomato paste factory), and omitting it as a unwanted provider a breeding place for a variety of pests such as flies and mosquitoes, which host of disease-causing organisms. The perception is the tomato pomace by many functional groups probably can be a very valuable adsorbent that is able to reduce the hazardous heavy metals Nickel and Cobalt from the effluent of pharmaceutical laboratories. The novelties of study are:

1- Utilizing green and natural bio-adsorbent regaining the considerable potential of food waste using it as a source of many green products, and opening up the possibility of their extraction and purification;
2- Using new methods and assistance in solving the agricultural/Food waste problems by government agencies can greatly help reduce heavy metals pollution and improve the production cycle.

## 2. Materials and Methods; Batch studies; Material preparation

Tomato pulp, pomace and seeds residue were collected from recognized Tomato paste Industries in Tehran country in August and September 2020. They were cut into small pieces (0.5-1cm), Tomato pomace and waste were high-moisture products: often when moisture is more than 80% up to 98% they could be spoiled very quickly, in less than 2 days in some cases, therefore they were prepared immediately after manufacturing processing and drying naturally in a room temperature for 18 hours. Then dried for 48 hours at 50 ° C to be stabilized and stop enzymatic reactions.Thereafter, the samples were subjected to a crusher to reduce particle sizes and then dried again for 4 hours at 65°C. The Tomato residue samples were used during the Bio-adsorption study at natural state with no chemical or thermal treatment.

### *Estimation of Heavy Metals in Effluents*

All the chemicals used in this work were of analytical grade and actual Pharmaceutical effluent and waste water samples were collected in 8 groups of 5L bottles from Chemical Laboratories (Inorganic Chemistry, Analytical Chemistry, General Chemistry, Organic Chemistry) from Pharmaceutical Chemistry Faculty in Tehran Medical Sciences, Islamic Azad University in Tehran, Iran. After collection, the wastewater effluent was instantly transported to the main research laboratory for analysis. Physico-chemical parameters such as pH, Dissolved oxygen, Total Solids, Total hardness, Electrical Conductivity, Total Dissolved Solids, Chloride, Sulphate, Calcium, Sodium, Cadmium, Lead, Nickel, Zinc, Copper, Chrome, Manganese ,Iron and Potassium were analyzed as per the standard methods (AOAC, 2001; Zahirnejad *et al.*, 2017; Shahsavan-Davoudi & Ziarati, 2020; Arabian *et al.*, 2020).

The synthetic Sigma-Aldrich stock solutions of $Ni^{+2}$ and $Co^{+2}$ (1000mg/L) were used for making standard solutions. The desired concentrations of six standard solutions for the each metal were prepared by successive dilutions of the stock solution (Ziarati *et al.*, 2016b).

20 mL of each waste water samples added to 3.0 ml concentrated HNO3 (65%, Merck) and cover beaker with watch glass or place a funnel in the mouth of digestion tube and allow to stand overnight or until frothing subsides. Placing covered beaker on hot plate or digestion tube into block digester and heating it at 95°C for 1 hour. Then the digestion tube was removed and it was let out to cool. Added 1 to 2 ml $H_2O_2$ 30% (Merck) due to organic compounds of tomato to stop enzymatic reactions would not affected to the analyses (Ziarati and Ghasemynezhad-Shanderman, 2014).

All recoveries of the metals observed exceeded 95%. Ni and Co ion concentrations were determined in three replications by means of Varian Vista ICP-MS device. The intra-day (for samples collected during the same day) and inter-day (for samples collected during different days) precision and accuracy of the method were determined under the optimal working conditions by triplicate measurements of known Ni/Co concentrations. The first standard stock solutions showed a 100.0 mgl/Lit concentration of Nickel (II) Nitrate, and Cobalt (II) Nitrate and aqueous standard solutions were prepared from it by means of appropriate dilution with 10% nitric acid. To determine Nickel and Cobalt concentrations by ICP-Mass after specific times, the wet digestion method were used (Zahirnejad *et al.*, 2017; Shahsavan-Davoudi & Ziarati, Mandel & Mandel, 2015). The samples were analyzed by NexION 300X ICP-MS (Perkin-Elmer, USA). The instrumental operating conditions for the determination of the elements were performed as analytical official methods (Tajik *et al.*, 2020).

### *Adsorbent particle size*

The crusher sieve was used for the reduction of particle size of the dried Grapefruit peel samples and for particle size distribution, respectively. The sieves were mechanically vibrated for 15 minutes, which was sufficient for separation to take place. The screens were subjected to weighing balance before and after the vibration to get the mass and size of the banana peel particles retained on each sieve. The particle size range used in this study was 0.15 mm to 3 mm.

***Biochemical oxygen demand (BOD)***

For Biological Oxygen Demand, 15 samples were processed after collection immediately for the determination of initial oxygen and incubated at 20°C for 5 days for the determination of BOD5 [49] .All the experiments were carried out in triplet and the relative standard deviation was less than 2%. In general, the sorption consisted of 0.1, 0.2, 03, 0.4, 0.5, 0.6, 1 and 2% for the adsorbent dose in one Liter of Pharmaceutical effluent and waste water samples were studied while for 0,48 and 72 hours, 1 and 2 week(s) without and stirring and for other samples at an agitation rate of 200 rpm with an adsorbent time of 1 week and 2 weeks at room temperature (25 ± 3). To study the effect of pH on sorption, the pH of the metal ion solution was adjusted to values in the range of (2–10) prior to the experiment. The Langmuir isotherms were obtained by equilibrating metal ion solutions of different adsorbent doses (1–20) mg/l with different times (0–2 weeks) at equilibrium pH and rpm with an initial metal concentration of 10 mg/l at room temperature.

***Total dissolved solids (TDS)***

The total solid concentration in waste effluent represents the colloidal form and dissolved species. The probable reason for the fluctuation of value of total solid and subsequent the value of dissolved solids due to content collision of these colloidal particles. The rate of collision of aggregated process is also influenced by PH of these effluents (Zahirnejad *et al.,* 2017; Shahsavan-Davoudi & Ziarati, 2020; Arabian *et al.*, 2020).

***Chemical oxygen demand (COD)***

The chemical oxygen demand test (COD) determines, the oxygen required for chemical oxidation of organic matter with the help of strong chemical oxidant. The COD is a test, which is used to measure pollution of domestic and industrial waste. The waste is measure in terms of equality of oxygen required for oxidation of organic matter to produce $CO_2$ and water. It is a fact that all organic compounds with a few exceptions can be oxidizing agents under the acidic condition. COD test is useful in pinpointing toxic condition and presence of biological resistant substances. For COD determination samples were preserved using $H_2SO_4$ and processed for COD determination after the entire sampling operation was complete (Zahirnejad *et al.*, 2017; Shahsavan-Davoudi & Ziarati, 2020; Arabian *et al.*, 2020).

***Statistical Analysis***

All experiments were performed 3 times and 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).

These values were compared and evaluated by Duncan's multiple range tests at 95% level and *p*-value less than 0.05. Variables studied in this study, the rate of reduction of heavy metals: Nickel and cobalt in laboratory effluents due to contact with tomato pomace powder as bio-adsorbent at different studied times have been determined by ICP-Mass. So the variables are as follows:

**Time**: is a dependent variable and its scale is of quantitatively continuous type.

**Bio-adsorbent concentration**: It is a dependent variable and its scale is slightly continuous.
Investigation on efficacy of bio-sorbent along with the presence of **stirring** and without stirring: It is a dependent variable and its scale is of nominal qualitative type.
**pH**: is a dependent variable and its scale is of slightly quantitative type.

## 3. Results

Chemical compositions of the wastewater effluent of studied Educational laboratories profile in pharmaceutical Chemistry faculty before treatment by Tomato pomace are shown in the table 1. Data is the mean of the effluent profiles.

**Table 1.** Characteristics of Wastewater from Chemical Laboratories in Pharmaceutical Chemistry Faculty, before treatment

| **Parameters** | **Concentration Range** |
|---|---|
| pH | 4.03 |
| BOD5 at 208 C (mg/L) | 3106 |
| COD (mg/L): chemical oxygen demand | 6680 |
| TSS (mg/L): total suspended solids | 52 |
| Total alkalinity as $CaCO_3$ (mg/L) | 94 |
| Lead (mg/L) | 4.832 |
| Nickel (mg/L) | 183.54 |
| Mercury (mg/L) | 0.09 |
| Zinc (mg/L) | 14.64 |
| Cobalt (mg/L) | 73.45 |
| Chromium (mg/L) | 3.15 |
| Chloride (mg/L) | 8.659 |
| Sulfide (mg/L) | 1.032 |
| Nitrate (mg/L) | 8718 |

As compared to BOD, COD was very high which is normal for effluent of such chemistry laboratories as the excess of 2000 students are studying pharmaceutical chemistry and applied chemistry as bachelor degree programs along with 100 students in master and PhD degree in pharmaceutical Chemistry faculty's laboratories. The mean content of BOD from 10 sub-samples was 3106 and the mean values of COD were 6680 mg/L for the sub-samples of studied effluent.

Wastes from chemical laboratories due to educational syllabus and projects and wet/acid digestion methods had acidic state contributed 50% of the total waste flow at 3700 mm3 /day and had a mean pH of 4.03 as is shown in table 1. The combined Analytical and Inorganic chemistry laboratories waste had a pH of 4.7 (including acidic waste stream), whereas the pH of the waste of Educational and research laboratories on the whole was 3.37.
Some heavy metal contents such as Cadmium in the wastewater were found to be much higher than the limits according to IS-3306 (1974). Most of the solids present were in a dissolved form, with practically no suspended solids.

This investigation was carried out to determine the accumulation of heavy metal: Nickel and Cobalt in Tomato Pomace waste (TPW) in contaminated waste water by heavy metals result in educational laboratories in Faculty center, chemical and toxicology laboratories' pharmaceutical effluent and wastewater after treating by Bio-adsorbent in different specific times and dose of adsorbents along with stirring factor.

All experiments were performed 3 times and SPSS-20 software was used to analyze the variance of the data. The means were compared and evaluated by Duncan's multiple range tests at 95% level and $p< 0.05$.

In all figures, SE stands for Standard Error, and the Latin lowercase letters indicate the significant difference between the data.

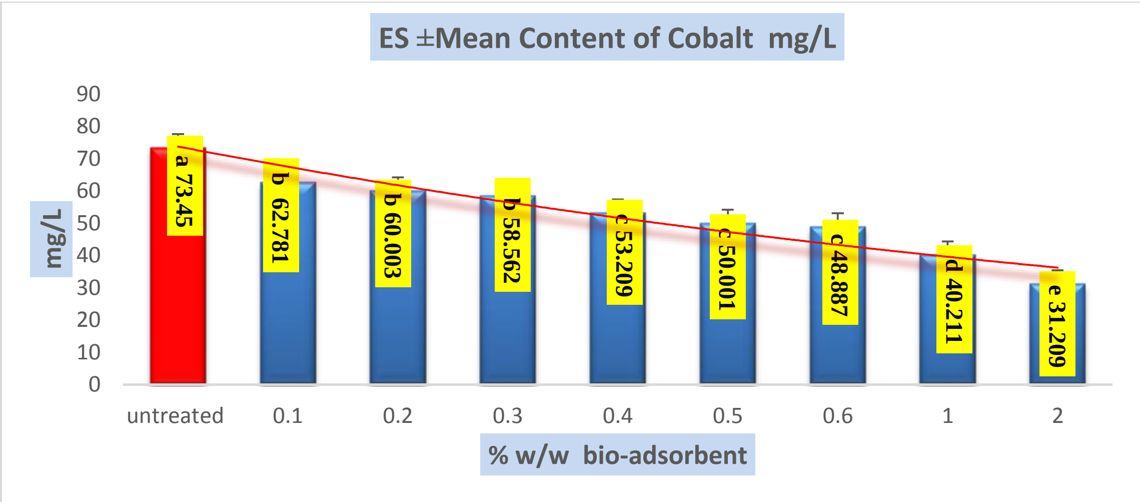
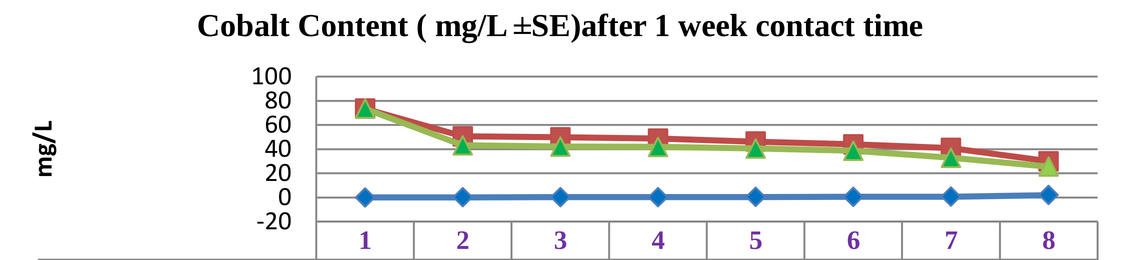



**Fig. 1.** Effect of 48 hours contact time on the removal of Cobalt from waste water (initial Co concentration=73.45 mg/L , bio-adsorbent doses=0.1, 0.2, 0.3,0.4, 0.5, 0.6. 1 and 2% Tomato pomace waste, temperature=25 ± 2ºC
SE* = Standard Error, and the Latin lowercase letters indicate the significant difference between the data

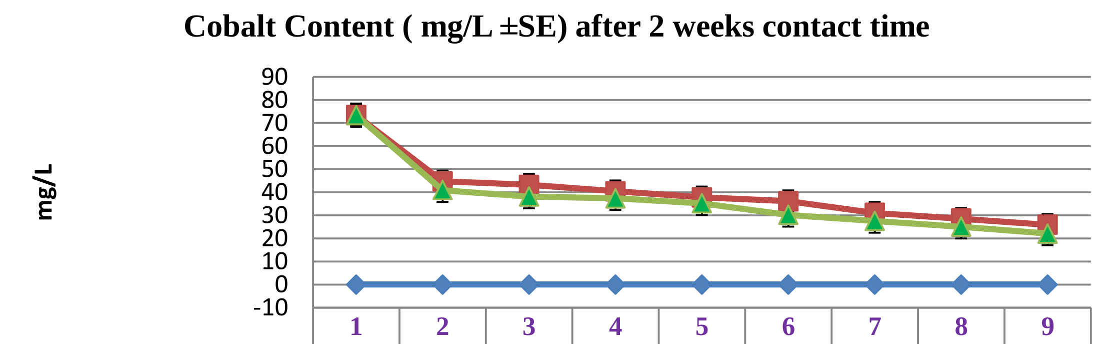
Results from figure 1 revealed that Tomato residue has significant potential to adsorb Cobalt ($p<0.05$) during 48 hours even in very low content of bio-adsorbent (0.1% w/w). In presence of 0.4,1 and 2% (w/w) the adsorbing process increased significantly during first hours of investigation. After 48 hours contact time in presence of 2% of TPW, reduction of Co was highly significant ($p<0.001$) and mean content of 73.45±1.01 dropped to 31.209 ±0.78 mg/L ±SE, that approved the adsorption capacity varied by considering the effects of various parameters like adsorbent dose.

The results of the increasing adsorbent to 0.6% ( mg TPW /100 milt waste water, in figure 2, showed significant differences in Cobalt up -taking by bio-adsorbent after 1 week with and without stirring factor. But despite of other previous concentration it can be observed that passing time up to 1 week has no significant difference by 72 hours ($p \geq 0.05$) and also 7 days (1 week) with stirring by 2 weeks without stirring too (comparing data in figure 2 and 3). The data showed that accomplishing of agitation speed= 200 rpm during 1 week (7 days) with stirred have significant differentiate ($p <0.05$). Cobalt content in untreated sate 73.54 mg/Lit after 1 week decreased to 40.504 mg/Lit by 0.5% concentration of biomass. This content of adsorbent can reduce 29.871 mg/Lit Cobalt in solutions without stirring while by stirring the wastewater solution in the presence of biomass it decreased to 25.414 mg/Lit in pharmaceutical effluent which means removal of % 69.98 of Cobalt. In figure 2, the manifest removal trend is observed.




| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|
| Bioadsorbent % | 0 | 0,1 | 0,2 | 0,3 | 0,4 | 0,5 | 0,6 | 2 |
| 1 Week | 73,45 | 50,542 | 49,802 | 48,713 | 46,209 | 43,982 | 40,873 | 29,871 |
| 1 Week + stirred | 73,45 | 43,222 | 42,094 | 41,872 | 40,504 | 38,721 | 32,891 | 25,414 |

**Fig. 2.** Effect of 1 week contact time, with stirring factor on the removal of Cobalt from waste water (initial Co concentration=73.45 mg/L , bio-adsorbent doses=0.1, 0.2, 0.3,0.4, 0.5, 0.6. 1 and 2 mg TPW /100 milt waste water, temperature=25 ± 2 ºC, agitation speed= 200 rpm), pH = 4.0
SE* = Standard Error, and the Latin lowercase letters indicate the significant difference between the data




| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|
| Cobalt Content | 0 | 0,10% | 0,20% | 0,30% | 0,40% | 0,50% | 0,60% | 1% | 2% |
| 2 weeks | 73,45 | 44,761 | 43,201 | 40,441 | 37,809 | 36,118 | 31,098 | 28,541 | 25,889 |
| 2 weeks + stirring | 73,45 | 40,908 | 38,169 | 37,413 | 35,207 | 30,242 | 27,604 | 25,098 | 22,098 |

**Fig. 3.** Effect of 2 weeks contact time, with stirring factor on the removal of Cobalt from waste water (initial Co concentration=73.45 mg/L , bio-adsorbent doses=0.1, 0.2, 0.3,0.4, 0.5, 0.6. 1 and 2 mg TPW /100 milt waste water, temperature=25 ± 2 ºC, agitation speed= 200 rpm), pH = 4.0
SE* = Standard Error, and the Latin lowercase letters indicate the significant difference between the data

Results in figure 3 in presence of bio-adsorbent doses=0.1, 0.2, 0.3,0.4, 0.5, 0.6. 1 and 2 mg TPW /100 milt waste water showed significant difference in Cobalt up-taking by bio-adsorbent after 14 days (2 week) with and without stirring. The data showed that accomplishing of agitation speed =200 rpm during 14 days (2 weeks) without stirred have no significant differentiate ($p \geq 0.05$) just like 1 week contact time while the stirring factor in the same concentrations of adsorbents in this study lead to significant boosting of removal heavy metal process, and the potential of taking up Cobalt was increased significantly between 2 week with agitation speed by 2 weeks in statistic state ($p<0.001$).

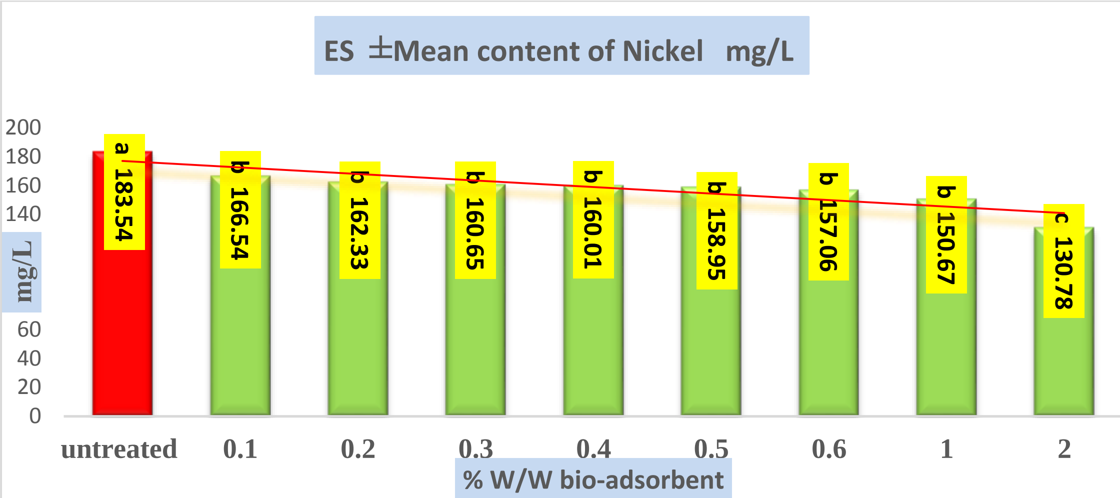
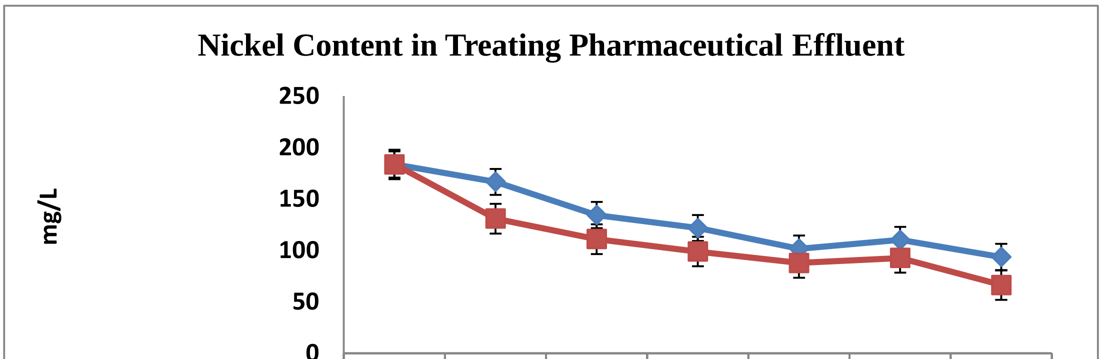



**Fig. 4**. Effect of 48 hours contact time on the removal of Nickel from wastewater (initial Ni concentration=183.54 mg/L, bio-adsorbent doses=0.1, 0.2, 0.3,0.4, 0.5, 0.6. 1 and 2 mg TPW /100 milt waste water, temperature=25 ± 2 ºC

SE* = Standard Error, and the Latin lowercase letters indicate the significant difference between the data

Results from figure 4 revealed that Tomato residue has significant potential to adsorb Nickel ($p$<0.05) during 48 hours even in very low content of bio-adsorbent (0.1 % w/w). In presence of 2% (w/w) the other significant decreasing was observed: the adsorbing process increased significantly during first hours of investigation and after 48 hours contact time in presence of 2% of TPW, reduction of Ni was significant (p<0.03) and mean content of 183.54±1.00 decreased to 130.78±0.11 mg/L ±SE. This approved the adsorption capacity of Nickel is not as much as its potential for Cobalt metal.




| | untreated samples | 48h | 72h | 1week (stirred solution) | 1week | 2week (stirred solution) | 2week |
|---|---|---|---|---|---|---|---|
| 0.1% bio-absorbent | 183,54 | 166,54 | 134,28 | 121,71 | 101,54 | 110,09 | 93,48 |
| 2% bio-absorbent | 183,54 | 130,78 | 110,83 | 98,76 | 87,65 | 92,61 | 66,21 |

**Fig. 5.** Effect of contact time, with stirring factor on the removal of Nickel from waste water (initial Ni concentration=183.54 mg/L, bio-adsorbent doses=0.1, 0.2, 0.3, 0.4, 0.5, 0.6. 1 and 2 mg TPW /100 milt waste water, temperature=25 ± 2 ºC, agitation speed= 200 rpm), pH = 4.0

SE* = Standard Error, and the Latin lowercase letters indicate the significant difference between the data

All concentrations were expressed on the basis of (mg / lit ± SE) in figure 5, ANOVA analysis showed that there was a significant difference ($p$ <0.02) in the concentration of nickel in the effluent of pharmaceutical laboratories with bio-sorbent 2% of TPW on different time contact. A dramatically decreasing in Ni concentrations is seen from 183.56±1.14 to 66.21 ±0.09 mg/L ±SE.

Results in figure 3 in presence of 0.1% and 2% Tomato Pomace showed almost the same results for removal of Cobalt but in lower trend and it can be concluded that this bio-adsorbent can accumulate selectively more Cobalt than nickel ions with the same content of bio-adsorbent. Moreover, time factor of putting adsorbent in contaminated effluent wastewater by Nickel in the study showed significant effect ($p < 0.05$) in the stirring solutions in the same contact time and bio-adsorbent contents.

This content of adsorbent can reduce up to 183.54 mg/Lit Nickel in untreated samples. While after 48 hours with biomass of TPW, it decreased to 130.78±1.01 mg/100 milt ± SE ($p<0.05$). After 2 weeks without stirring this content dropped dramatically to 66.21±0.06 mg/100 milt in waste water solution and in the presence of biomass along with stirring factor it decreased to 25.414 mg/Lit in pharmaceutical effluent which means removal of %63.93 of Nickel in figure 5, the manifest removal trend in this green method is observed.

## 4. Conclusion

Today, there is a general lack of accurate information and understanding of the extent of food waste in different areas—phases of the food value chain from farm to fork. Scale Food waste is complex across of the food supply chain .It can have a huge impact on a number of different ways, such as agriculture, food security, economics, waste Use and management, environmental protection, and human health. Current research is suggested for the characterization of novel bio-adsorbents from other waste of herbal plants, agriculture/food-industry with maximum heavy metals sorption capacities to promote large-scale use of bio-adsorbents.

The intention of using bio-sorbents could be helpful in the development of an affordable ‘green environmental technology for purification of heavy metals-contaminated drinking water which could present low income communities to savor heavy metals-free drinking water to protect them from health hazards and toxics.

The current green study showed that by TPW biomass, %63.93 of Nickel and % 69.98 of Cobalt can easily remove from Pharmaceutical contaminated effluent.

The heavy metals contamination is more prevalent due to inefficient food regulatory policies, inadequate environmental monitoring, and enforcement strategies. The health implications of trace elements and the toxic consequences of heavy metals necessitate effective monitoring of food products to ensure the public health safety.

he decreasing level of Co contents trend even in contaminated wastewater by Tomato Pomace waste ( TPW) as bio-adsorbent showed that probably complicated functional group and molecules in TPW by chelating agents are rapidly excreted over a few hours or days. It can lead to building the firm complex and the chelating agents-ligands which are able to form two or more coordinate covalent bonds with a Cobalt metal ion. Further studies are required to increase the understanding about the adsorption mechanism at the bio-sorbent-water interface.

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**Conflicts of Interest**

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

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