Ecological Questions 32(2021)2 http://dx.doi.org/10.12775/EQ.2021.014

Kinetics of Cd, Co and Ni Adsorption from Wastewater using Red and Black Tea Leaf Blend as a Bio-adsorbent

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Received: 29 May 2020 / Accepted: 27 August 2020

Abstract. Every year there is deterioration in water quality. This is due to human activity. The current environmental strategies of many countries motivate the scientific community to develop reliable, economically viable and environmentally friendly technologies that are able to remove pollutants from the environment, including water. The study purpose is to determine of influence regularity of the bio-adsorbent composition and amount, which consists of red and black tea leaves mixture, on the Cd, Co and Ni adsorption process based on experimental data. As well as determine the most rational bio-adsorbent dose and the necessary red and black tea dose in bio-adsorbent to achieve MPC of heavy metals, with which process duration will be minimal. Initially, to study the adsorption process kinetics, the nature of the curve that describes the obtained experimental values was visually analyzed. To determine the adsorption process kinetic regularity, which most adequately and reliably describes the experimental data and to determine the values of the coefficients in the exponential regularity, the least squares method was used. It was observed that for Cd and Co, an increase in the black and red tea amount leads to a drastic reduction of the adsorption process time (up to 10 times); while for Ni the black tea addition slows down the adsorption process. Ni adsorption is the most complex and for certain bio-adsorbent composition values, complete Ni removal cannot be achieved in a technologically reasonable adsorption time. The technological process of Cd, Co and Ni adsorption can be expedient, if it is carried out in several stages with optimal red and black tea amounts for each of the metals. Adsorption process kinetic regularity, which was determined, can be used to calculate of adsorption process technological parameters in values wide range.

Keywords: kinetic regularity of adsorption, bio-adsorbent dose, leaves, heavy metals, wastewater.

1. Introduction

Every year there is deterioration in water quality. This is due to human activity (Kipigroch et al., 2012; Malovanyy et al., 2018; Kolesnyk et al., 2016), population growth (Cheevaporn & Menasveta, 2003; Jiang, 2009), rapid industrialization (Jiang, 2009) and toxic substances leakage through the soil layers (Parzych et al., 2013; Vambol et al., 2018; Vambol et al., 2019). The current environmental strategies of many countries motivate the scientific community to develop reliable (Bobik et al., 2017), economically viable (Jutsz & Gnida, 2015; Khan et al., 2019) and environmentally friendly technologies that are able to remove pollutants from the environment, including water.

A variety of wastewater treatment technologies are currently available, but with success varying degrees at monitoring and minimizing water pollution (Terentiev et al., 2018; Ölmez & Kretzschmar, 2009). The main disadvantages of most of these methods are the high maintenance costs, the formation of toxic sludge and the water treatment complicated technology (Bhatnagar et al., 2015). Compared with other processes, the adsorption process is the best alternative for water and wastewater treatment, because it is convenient, easy to operate and simple in design (Bhatnagar et al., 2015; Ali et al., 2012; Gautam et al., 2014). Although, in some cases, is arising need of the adsorbent regeneration or sorbent utilization which has expired (Gautam et al., 2014; Terentiev et al., 2016). And this is often a problem.

In the conditions of the need for rational natural resources use and reducing financial costs, scientists are actively engaged in the useful features study of by-products from various activities such as agriculture and industry. If this waste can be used as an inexpensive adsorbent, it will provide a twofold advantage for environmental protection. Considerable attention is paid to the adsorption properties of food waste and their use to remove various pollutants from water, such as heavy metals (Gambhir et al., 2012; Ziarati et al., 2018). Firstly, the volume of by-products (or waste) can be partially (or much) reduced, and, secondly, a cheap adsorbent, if it is developed, can reduce pollution of wastewater at a reasonable price (Grassi et al., 2012). In addition, the use of organic sorbents and bio-adsorbents makes it possible to more effectively purify natural and waste waters from heavy metal ions (Yadanaparthi et al., 2009; Pourzare et al., 2017).

In a study (Patent CN107129001, A), the authors proposed the use of black tea powder to extract lead ions. This method advantage is the almost complete metal ions removal from the solution at low temperatures and within an acceptable time interval. But the disadvantage of this method is that the adsorbent uses tea powder, which is more expensive than other bio-adsorbents. In addition, due to the small size of the adsorbent particles, there are problems with its subsequent removal. In this case, some of the organic matter (primarily the phenol compounds) are permeating into solution and contaminating of the treated water by organic compounds.

As was shown in our previous studies, one of the promising areas for the heavy metal compounds removal from wastewater is the use of bio-adsorbent from a mixture of black and red tea (*Hibiscus sabdariffa* L.) leaf waste (Ziarati et al., 2018). The advantages of this bio-adsorbent, unlike others, unlike others (Ziarati et al., 2019):

– Accessibility and cheapness, since it is itself a waste;

– Tea leaves contain almost no organic substances that can contaminate into solution;

– The organic substances presence of tea leaves that very strongly bind heavy metal ions;

– Waste leaves have the shape and size that are most beneficial for adsorption, and the heavy metals removal from the solution;

– Disposal of such an adsorbent can be carried out by known methods that do not require sophisticated equipment.

From the conducted studies it was found that the removal of compounds of heavy metals is almost 100% and they do not desorbed to the solution even at high temperatures. The amount of adsorbed metals is proportional to the adsorption time, which allows you to determine the minimum time of the adsorption process (Ziarati et al., 2019).

Given the above, the introduction of metal adsorption technology based on the use of a bio-adsorbent from a mixture of black and red tea wastes is of great interest on an industrial scale. Therefore, it is necessary to assess the feasibility of implementing such technology. In this case, important technological parameters are the initial and final concentration of heavy metals, the contact time of the adsorbent with contaminated water, the adsorbent amount (black and red tea) and the ratio of the black and red tea amount in the composition of the bio-adsorbent.

Therefore, the study purpose is to determine of influence regularity of the bio-adsorbent composition and amount on the heavy metals adsorption process. Namely, the adsorption kinetics of cadmium, cobalt and nickel from contaminated water was studied in order to determine the most rational bio-adsorbent dose and the necessary red and black tea dose in bio-adsorbent to achieve MPC if the initial concentrations of heavy metals are known. By rational bio-adsorbent dose and composition we understand an amount at which the metal concentration decreases to the MPC in a minimum time.

2. Materials and Methods

The initial concentration of heavy metals, such as cadmium, cobalt and nickel, in untreated wastewater, as well as treated with *Hibiscus sabdariffa* L. sepals in addition to the residue of black tea, was analyzed. At time intervals: 1, 5, 10, 15, 30, 40 minutes (with stirring), the final concentration of heavy metals in the samples was analyzed using atomic absorption spectroscopy. Samples were analyzed using 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. The average of five values is fixed. Data were tested 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 bio-adsorbent from a mixture of black and red tea leaf waste. 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) (Ziarati et al., 2018).

This study is based on a statistical synthesis of the experimental data results and patent research, which were presented in previous publications (Ziarati et al., 2018; Ziarati et al., 2019).

Initially, to study the adsorption process kinetics, the nature of the curve that describes the obtained experimental values was visually analyzed. In this case, the experimental values for each experiment, then for a group of experimental data, then for the entire array of experimental data obtained were analyzed. Various groups of experimental data were formed for analysis:

- The group that combines experimental data obtained for different metals, but for same bio-adsorbent composition;
- The group that combines experimental data obtained for one metal, but for different bio-adsorbent compositions.

To determine the type of adsorption process kinetic regularity, which most adequately and reliably describes the experimental data, the least squares method was used. By a reliable and adequate regularity was understood a regularity in which the determination coefficient is the highest for all experimental data groups.

To determine the values of the coefficients in the exponential regularity, the least squares method was used for the entire data array. First, for each group, the coefficients were selected, then the general dependence was determined and the coefficients for the entire array were selected.

The following nomenclature was used in formulas, equations and calculation:

$C = C_B + C_R$ – total bio-adsorbent dose (bio-adsorbent concentration), g/100 ml;

C_B – black tea bio-adsorbent dose, g/100 ml;

C_R – red tea bio-adsorbent dose, g/100 ml;

$C^F{}_B = (C_B/C)100$ – percentage fraction of the black tea bio-adsorbent, %

$C^F{}_R = (C_R/C)100$ – percentage fraction of the red tea bio-adsorbent, %

$T = 25 \pm 1$ – solution temperature, ºC pH solution – pH = 3.5

C_{Me} – current metal concentration (Cd, Co, or Ni) into contaminated water (Eq. 1), mg/l

C_0 – initial metal concentration (Cd, Co, or Ni) into contaminated water (Eq. 1), mg/l

d_1 – percentage fraction of fast process (determined on basis of contact time relation) (Eq. 1), %;

τ_1 – characteristic time for the first part of contact time relation (Eq. 1), min

τ_2 – characteristic time for the first part of contact time relation (Eq. 1), min

d_1^{Cd} – percentage fraction of fast process for Cd removing (Eq. 2a), %;

d_1^{Co} – percentage fraction of fast process for Co removing (Eq. 2b), %;

d_1^{Ni} – percentage fraction of fast process for Ni removing (Eq. 2c), %;

τ_1^{Cd} – characteristic time for Cd (first part of contact time relation) (Eq. 3a), min

τ_1^{Co} – characteristic time for Co (first part of contact time relation) (Eq. 3b), min

τ_1^{Ni} – characteristic time for Ni (first part of contact time relation) (Eq. 3c), min

τ_2^{Cd} – characteristic time for Cd (second part of contact time relation) (Eq. 4a), min

τ_2^{Co} – characteristic time for Co (second part of contact time relation) (Eq. 4b), min

τ_2^{Ni} – characteristic time for Co (second part of contact time relation) (Eq. 4c), min

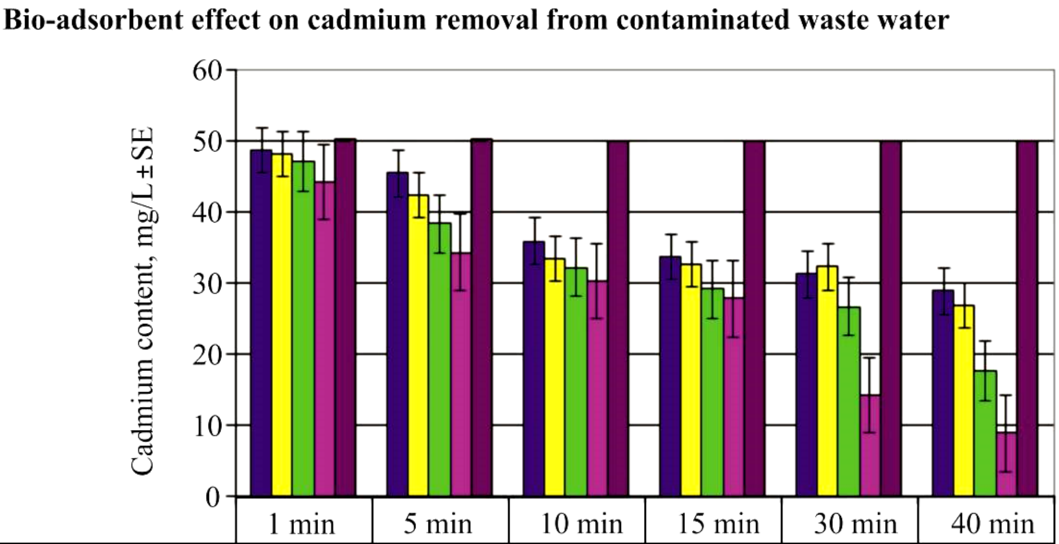
R^2 – determination coefficient

Δ – average error, %

τ – contact time of contaminated water with bio-adsorbent, min.

3. Results

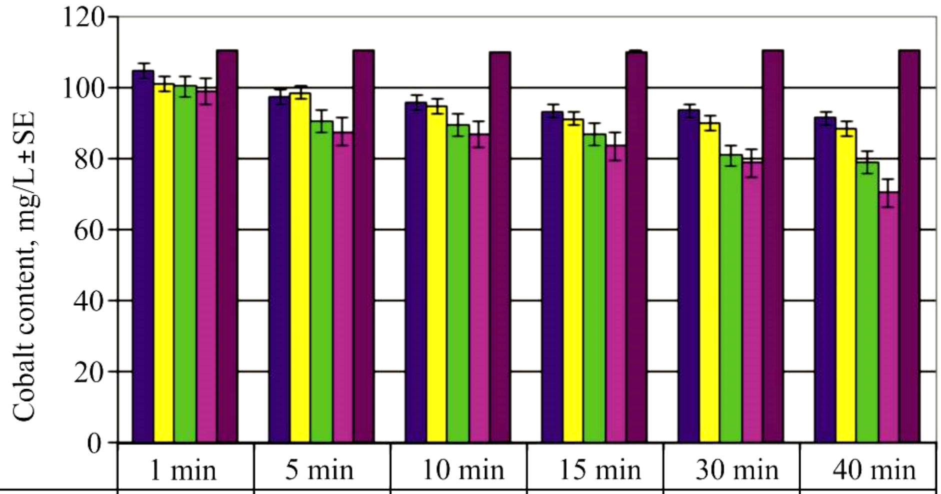
The results of study (Ziarati et al., 2018) revealed that heavy metals adsorption when using the bio-adsorbent from a mixture of black and red tea wastes ranged from 31…50% after agitation for 40 minutes (equilibration time). To study this problem, the bio-adsorbent with a different ratio of red and black tea was used; the amount of bio-adsorbent was also different. At the same time temperature was 25 ± 1 ºC, pH = 3.5. After the equilibration time a significant further increase of heavy metals adsorption was not observed ($p \geq 0.05$). Bio-adsorbent dose is one of the most important factors which affect significantly on influence specific uptake of all studied heavy metals: Ni, Cd and Co 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 (Fig. 1-3) (Ziarati et al., 2018).



	1 min	5 min	10 min	15 min	30 min	40 min
0.1% bio-adsorbent *H. sabdariffa L.* sepal + 1% black tea residue	48.54	45.312	35.787	33.552	31.102	28.779
0.2% bio-adsorbent *H. sabdariffa L.* sepal + 2% black tea residue	48.04	42.338	33.217	33.574	32.111	26.788
0.3% bio-adsorbent *H. sabdariffa L.* sepal + 3% black tea residue	47.03	38.195	32.067	28.974	26.571	17.454
0.5% bio-adsorbent *H. sabdariffa L.* sepal + 3% black tea residue	44.012	34.187	30.107	27.651	14.092	8.732
untreated contaminated effluent	50.032	50.021	49.868	49.866	49.964	49.866

Figure 1. Effect of contact time on the removal of cadmium (initial Cd concentration = 50.032 mg/l, T = 25 ± 1 ºC, pH = 3.5) (Ziarati et al., 2018)

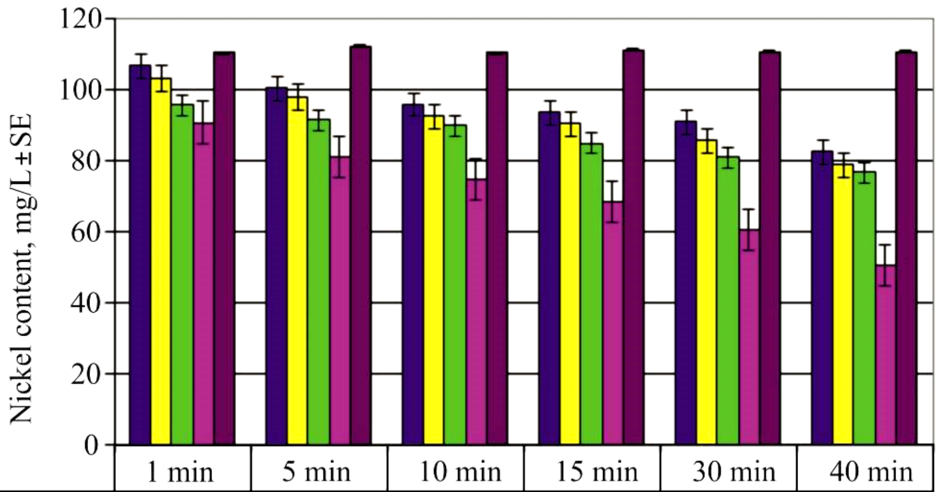
Bio-adsorbent effect on cobalt removal from contaminated waste water



	1 min	5 min	10 min	15 min	30 min	40 min
0.1% bio-adsorbent *H. sabdariffa L.* sepal + 1% black tea residue	103.422	97.106	95.602	93.116	93.217	91.181
0.2% bio-adsorbent *H. sabdariffa L.* sepal + 2% black tea residue	100.881	98.419	94.333	91.018	89.806	88.112
0.3% bio-adsorbent *H. sabdariffa L.* sepal + 3% black tea residue	100.001	90.154	89.094	86.731	80.556	78.667
0.5% bio-adsorbent *H. sabdariffa L.* sepal + 3% black tea residue	98.65	87.287	86.564	83.211	78.444	70.193
untreated contaminated effluent	110.21	110.45	109.89	109.988	110.23	110.35

Figure 2. Effect of contact time on the removal of cobalt (initial Co concentration = 110.21 mg/l, T = 25 ± 1 ºC, pH = 3.5) (Ziarati et al., 2018)

Bio-adsorbent effect on nickel removal from contaminated waste water



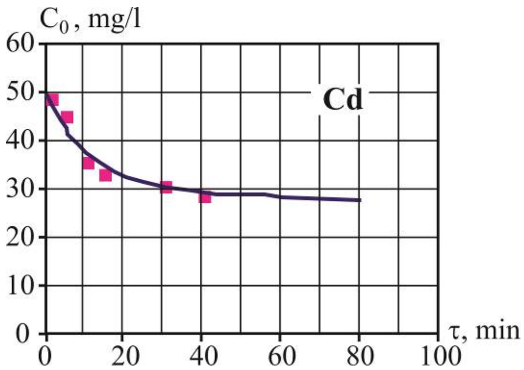
	1 min	5 min	10 min	15 min	30 min	40 min
0.1% bio-adsorbent *H. sabdariffa L.* sepal + 1% black tea residue	106.52	100.032	95.556	93.213	90.617	82.187
0.2% bio-adsorbent *H. sabdariffa L.* sepal + 2% black tea residue	102.889	97.632	92.206	90.111	85.345	78.432
0.3% bio-adsorbent *H. sabdariffa L.* sepal + 3% black tea residue	95.498	91.222	89.704	84.532	80.556	76.562
0.5% bio-adsorbent *H. sabdariffa L.* sepal + 3% black tea residue	90.478	80.778	74.306	68.092	60.232	50.320
untreated contaminated effluent	110.15	111.90	110.16	110.87	110.34	110.28

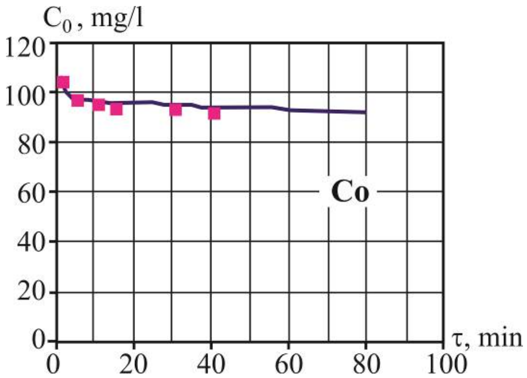
Figure 3. Effect of contact time on the removal of nickel (initial Ni concentration = 110.15 mg/l, T = 25 ± 1 ºC, pH = 3.5) (Ziarati et al., 2018)

Figure 4 and 5 showed examples of kinetic dependences for various bio-adsorbent amounts. Visual assessment of the kinetic dependency shape showed the presence of at least two parts on the chart, but two parts are very pronounced.

The first part of the graph shows a sharp decrease in the concentration of the corresponding metal by 5-10% of the initial value for 1-5 minutes. Thereafter, there is a slower decrease in concentration in the second part of the graph. Thus, the first part of the graph is characterized by a fast absorption process, which is observed up to 5 minutes (the fast process), and the second part is characterized by a slow absorption process that takes place after 5 minutes from the cleaning start (the slow process).

This form of kinetic dependence is characteristic of all experiments series; therefore, it can be considered as a general dependence for a adsorption process (Fig. 4, 5).





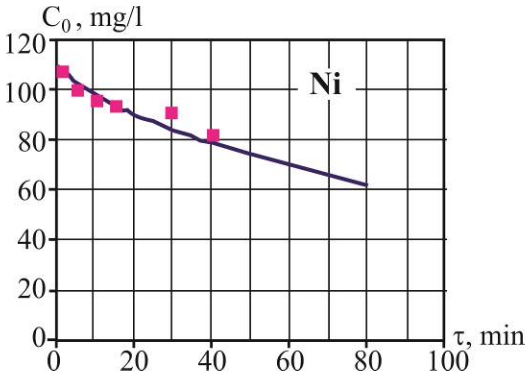


Figure 4. Some kinetic dependencies at at 0.1% percentage fraction of the red tea bio-adsorbent in accompany of black tea residue, T = 25 ± 1 ºC, pH = 3.5

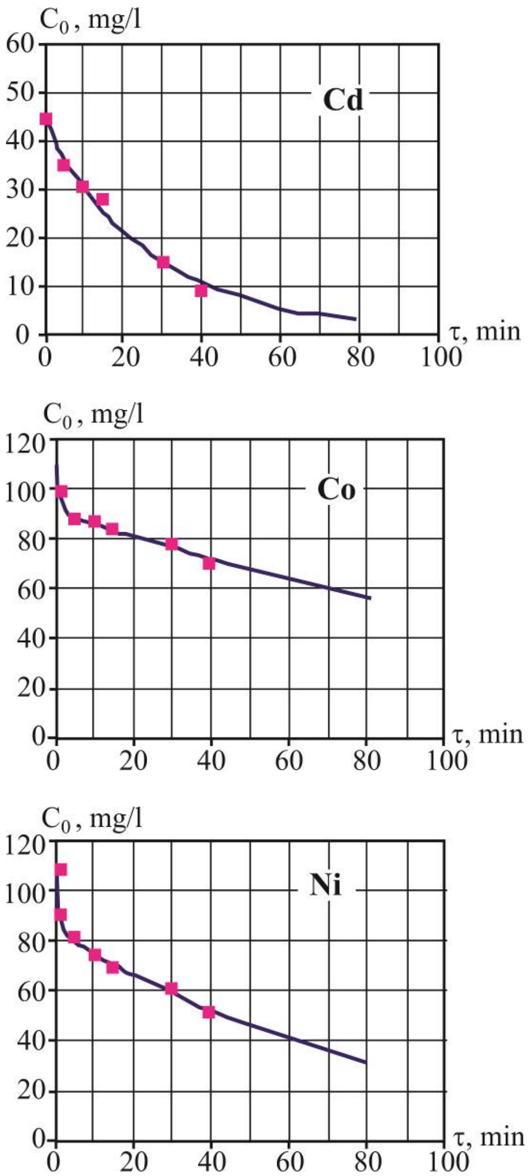


Figure 5. Some kinetic dependencies at 0.5% percentage fraction of the red tea bio-adsorbent in accompany of black tea residue, T = 25 ± 1 ºC, pH = 3.5

We accentuate that the presence of two different parts indicates that the reaction in the first part is not zero. Since with zero reaction, the kinetic dependence would have the straight line form. Therefore, this process is not due to physical adsorption, but by a chemical process. For the second part of graph, this conclusion is not unambiguous, since for some series of experiments the concentration dependence on time is close to linear. However, statistical processing of the entire data array showed that the dependence that is responsible for the first order of the kinetic equation is the most adequate. This means that for this part of the graph, adsorption is also determined by a chemical process. This statement is very important because it means that it is impossible to achieve the complete metal ions extraction even with a very long contact time of the bio-adsorbent with contaminated water. On the other hand, the reaction first order means that the adsorption rate depends solely on the metal ions concentration in the solution, that is, there is no change in the chemical adsorbent activity during the adsorption process.

Thus, the exponential regularity best describes all experimental data and the statistical generalization of the results of experimental research of the adsorption process was proposed in this form:

$$C_{Me} = C_0 \cdot \left[1 - d_1 \cdot e^{-\frac{\tau}{\tau_1}} - (1 - d_1) \cdot e^{-\frac{\tau}{\tau_{21}}} \right], \qquad (1)$$

where C_{Me} – current metal concentration in solution, mg/l; C_0 – initial metal concentration in solution, mg/l; d_1 – proportion of fast process in total adsorption process, %; τ_1 – time to concentration reduce of 2.72 times for the first part, min; τ_2– time to concentration reduce of 2.72 times for the second part, min.

It allows you to calculate the final metals concentrations values in the solution with their known initial values, the adsorption time and the adsorbent amounts. In this case, the determination coefficient R^2 = 0.95, and the average error Δ=±1.6%. Table 1 shows the values of the coefficients for equation (1).

Table 1. The values of the coefficients for equation 1 (all experiments series)

C_R	C_B	d_1	τ_1	τ_2	Δ
Cd					
0.1	1	0.395	10.831	650.04	1.80
0.2	2	0.335	6.558	243.94	2.10

0.3	3	0.254	3.863	63.12	2.09
0.5	3	0.145	1.019	27.88	1.71
Co					
0.1	1	0.123	1.647	726.12	0.85
0.2	2	0.114	0.830	362.93	1.72
0.3	3	0.162	1.274	242.72	0.64
0.5	3	0.173	1.158	170.50	1.55
Ni					
0.1	1	0.088	2.771	225.49	1.71
0.2	2	0.102	1.208	181.27	1.34
0.3	3	0.153	0.557	200.95	1.11
0.5	3	0.230	0.765	79.40	1.64

The table shows that the coefficient values for each experiment series are close to each other. This confirms the correctness of the proposed exponential regularity. The presences of regular coefficients changes depending on the bio-adsorbent concentrations and on its composition are also clearly visible from Table 1. This allows generalizing the coefficients:

$$d_1^{Cd} = 0.5072 \cdot e^{-2.418 \cdot C_R};$$
$$d_1^{Co} = 0.109 \cdot e^{0.966 \cdot C_R}; \qquad (2)$$
$$d_1^{Ni} = 0.06975 \cdot e^{2.405 \cdot C_R}.$$

For establish the dependence of the coefficient values on the adsorbent concentration were studied: linear, power, logarithmic and exponential functions. It was found that the smallest error is observed if we use the exponential function. In addition, it was found that the contribution share of the fast adsorption process is associated only with the red tea amount and does not depend on the black tea amount. This most likely indicates that in the absorption process the most important is red tea as a bio-adsorbent component.

The fast process share for cadmium decreases with an increase in the red tea amount, and for cobalt and nickel it increases. However, for all cases, the red tea amount does not exceed 30% of the adsorbent total capacity. The characteristic time (time during which the metal concentration decreases to 37% of the initial concentration) for this process also depends on the adsorbent amount, and in different measure for different metals:

$$\tau_1^{Cd} = 19.417 \cdot e^{-5.718 \cdot C_R};$$
$$\tau_1^{Co} = 1.2051; \qquad (3)$$
$$\tau_1^{Ni} = 7.656 \cdot e^{2.223 \cdot C_R} \cdot e^{-1.1313 \cdot C_B}$$

So for cadmium, the characteristic time decreases dramatically from 20 minutes to 1 minute with increasing red tea amounts, for cobalt it remains constant – about 1 minute, and for nickel it increases with increasing red tea amounts and decreases with the black tea addition. However, the most important is the effect of the adsorbent amounts on the slow process:

$$\tau_2^{Cd} = 2088.4 \cdot e^{-3.927 \cdot C_R} \cdot e^{-0.78075 \cdot C_B};$$
$$\tau_2^{Co} = 1740.8 \cdot e^{-0.9279 \cdot C_R} \cdot e^{-0.61074 \cdot C_B}; \qquad (4)$$
$$\tau_2^{Ni} = 245.1 \cdot e^{-4.134 \cdot C_R} \cdot e^{0.31655 \cdot C_B}.$$

So for Cd and Co, an increase in the black and red tea amount leads to a drastic reduction of the adsorption process time (up to 10 times), while for Ni the black tea addition slows down the adsorption process.

It should also be noted that the proposed dependences use for the coefficients of equation (1) practically does not reduce the calculations accuracy ($\Delta = \pm 1.68$).

4. Discussion

The feature of the statistical generalization of the results of experimental research, which includes equation (1) and equations systems (2)-(4), is the possibility of heavy metals adsorption process studying if water is contaminated by one metal type or by several types at the same time.

As can be seen from Figure 6, cadmium adsorption occurs most rapidly. After 2 hours, its concentration in the contaminated water becomes less than the maximum permissible concentration (MPC). To reach acceptable concentrations of Ni and Co, a longer contact time is required. Using small adsorbent amounts (up to 4%) this time can be 8-12 hours.

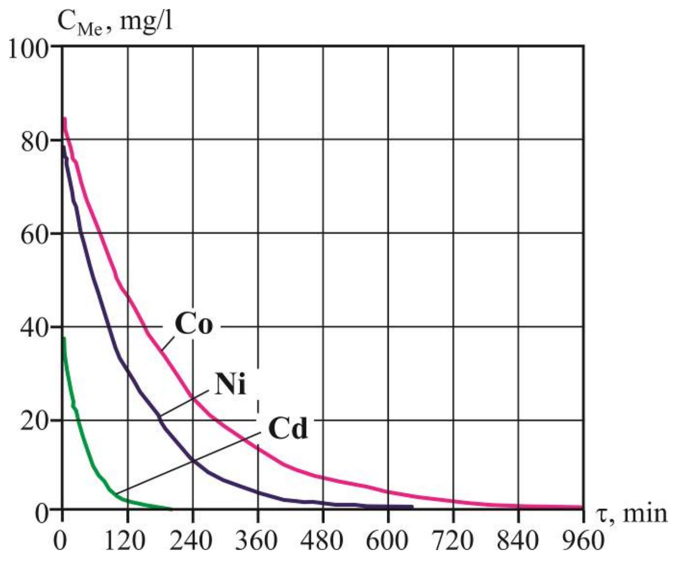


Figure 6. Dependence of heavy metals concentration in the contaminated water on the contact time with the adsorbent (initial concentrations of Cd – 50 mg/l, Co – 100 mg/l and Ni – 100 mg/l, adsorbent concentration – 0.4% red tea and 3% black tea)

The study also showed a fundamental difference in the influence of the adsorbent composition on the Ni adsorption degree. Unlike Co and Cd ions, increasing the black tea concentration reduces the Ni ion adsorption rate. As a result, we have the red and black tea concentrations, at which complete purification from Ni is practically impracticable (Fig. 7).

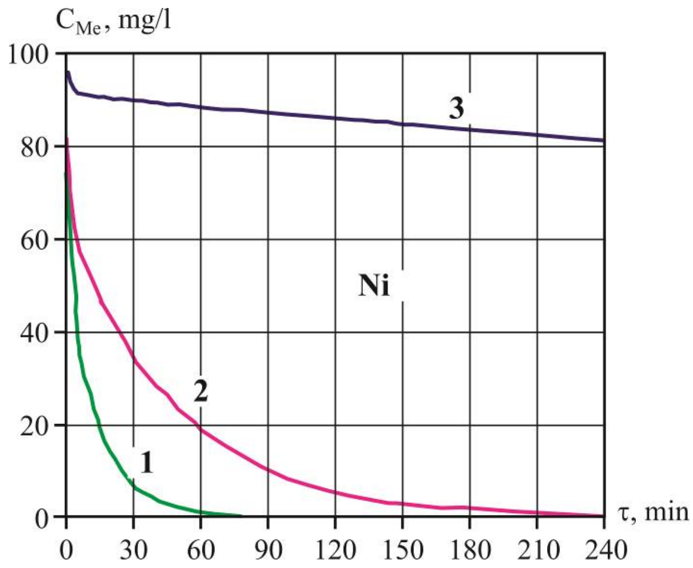


Figure 7. Dependence of Ni concentration in the contaminated water on time: 1 – 0.9% red tea and 3% black tea; 2 – 0.7% red tea and 4% black tea; 3 – 0.1% red tea and 8% black tea

From Figure 8 it can be seen that almost complete Cd extraction from the contaminated water is possible if the contaminated water contacts 30 minutes with an adsorbent containing 3% black tea and less than 1% red tea. A higher red tea concentration (more than 1.5%) will reduce the Ni adsorption, and to ensure the safe concentration of Co, the red tea concentration should be much higher than 2.5%.

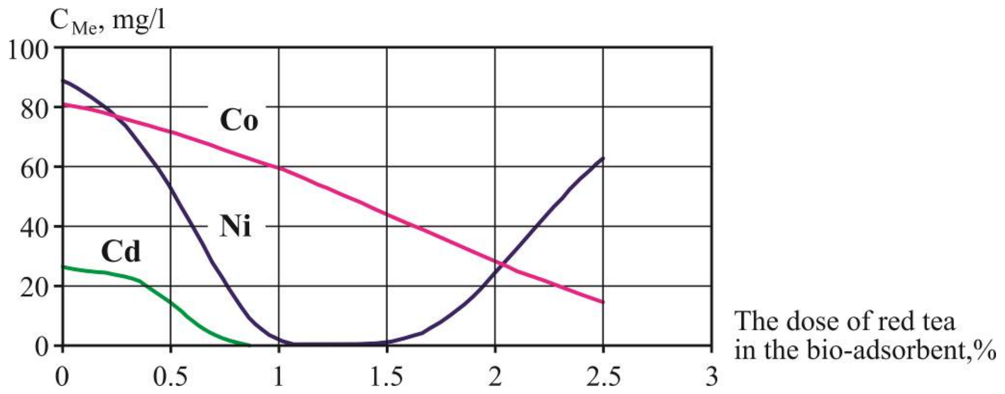
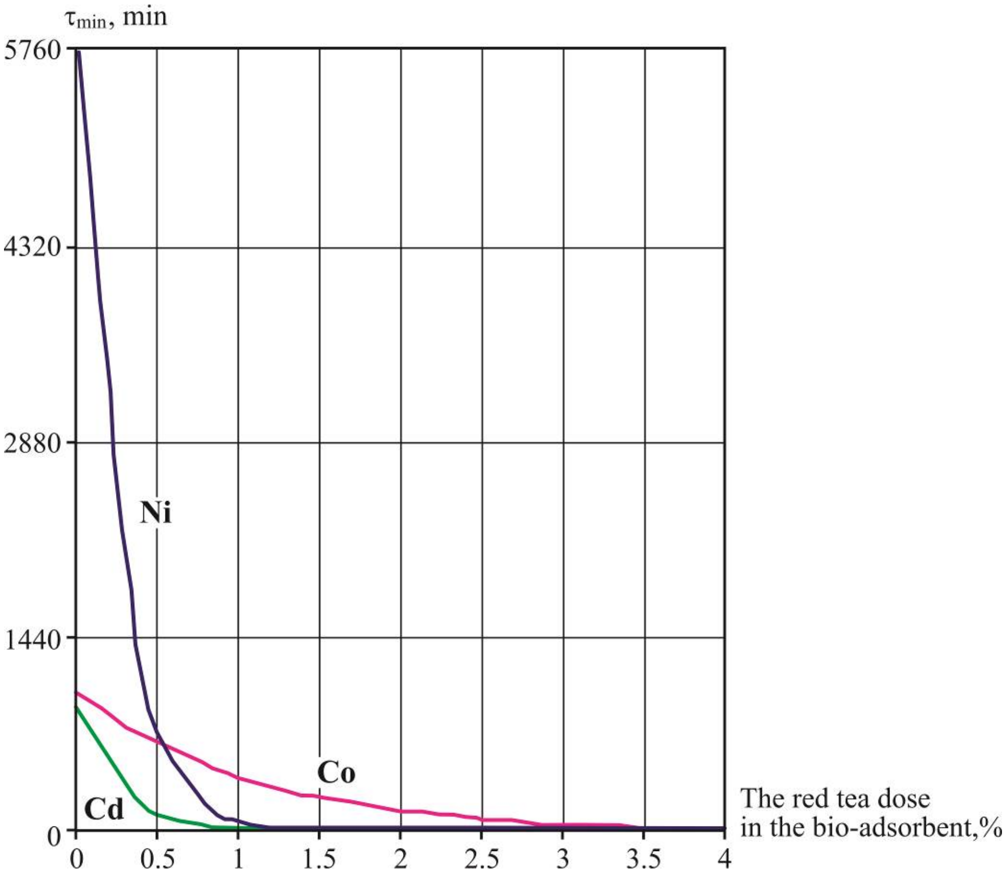


Figure 8. Metals concentration change in contaminated water at various doses of red tea in the bio-adsorbent (τ = constant), T = 25 ± 1 ºC, pH = 3.5

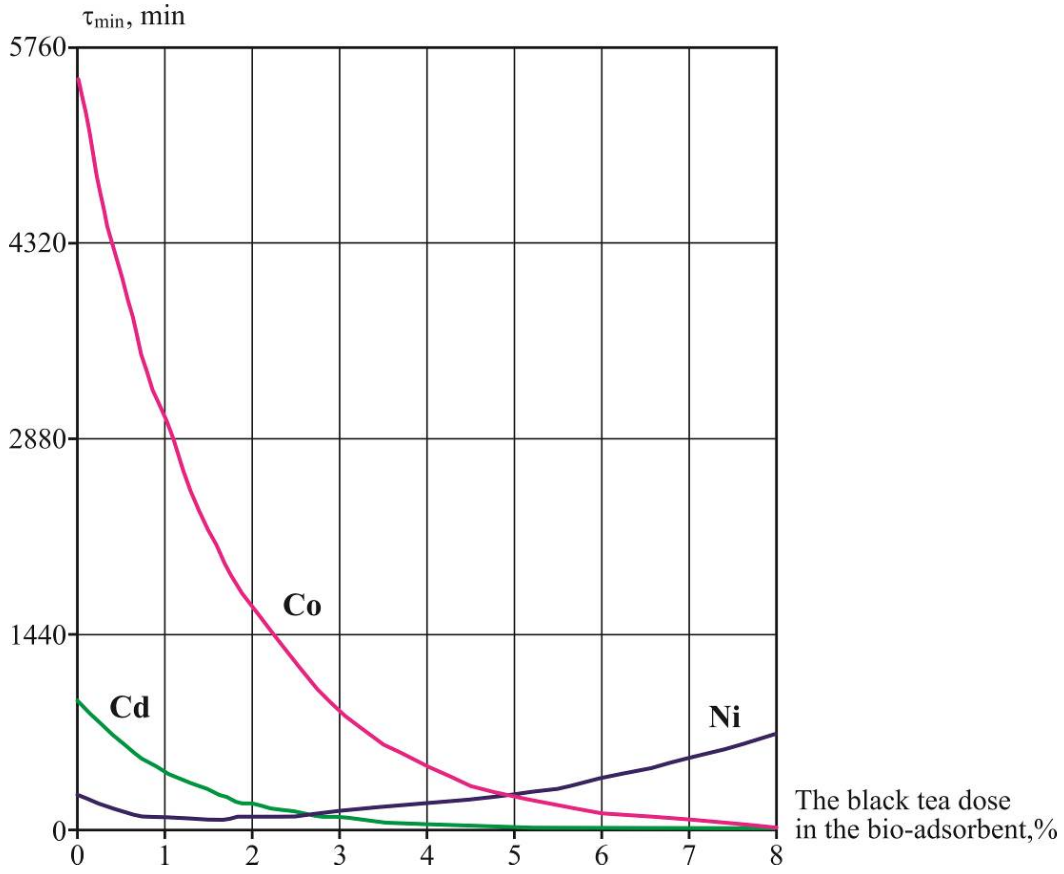
An important technological conclusion follows from this: the technological process of Cd, Co and Ni adsorption can be expedient, if it is carried out in several stages with optimal red and black tea amounts for each of the metals. The important advantage of this approach includes the contaminated bio-adsorbent treatment simplicity after its use.

From a technological viewpoint, water purification is not important until the complete metals removal, but to certain concentration. Therefore, it is required to determine the minimum necessary contact time of the bio-adsorbent with the contaminated water, during which the purification degree of contaminated water may be accepted as acceptable. That is, the heavy metals concentration in contaminated water will not exceed the maximum permissible concentrations values (MPC). A subsequent increase in contact time can be considered economically inexpedient.

According to equation (1), the adsorption degree depends on the contact duration of the bio-adsorbent with contaminated water. If we determine the minimum necessary adsorption time (i.e. contact duration of the bio-adsorbent with contaminated water at which the heavy metals concentration reached values that do not exceed the MPC) for given initial and final concentrations, then it can be easily recalculated for any other values. For the study of the adsorption process kinetic regularity, initial values of the heavy metal concentrations in contaminated water were accepted: Cd – 50 mg/l, Co – 100 mg/l, Ni – 100 mg/l. As the final values of the heavy metal concentrations in contaminated water, were taken MPC: Cd – 0.001 mg/l, Co – 0.1 mg/l, Ni –0.1 mg/l (Fig. 9).



a)



b)

Figure 9. Dependence of minimum necessary adsorption time on the red or black tea dose in the bio-adsorbent: a – the red tea dose is variable, the black tea dose is 4%; b – the black tea dose is variable, the black tea dose is 0.8%, T = 25 ± 1 ºC, pH = 3.5

As can be seen from Figure 9 an increase in the red tea concentration always results in a decrease in the minimum adsorption time. And at a concentration of more than 2.5%, the adsorption time for all metals less than 60 minutes. At the same time, an increase in the concentration does not lead to a monotonic decrease in the minimum adsorption time for Ni, but to dependence with a minimum. Moreover, the value of the minimum depends on the red tea concentration.

Figure 10 shows the dependence of the minimum necessary adsorption time of three metals simultaneously before reaching the MPC on the bio-adsorbent composition. In Figure 10, also seen the minimum necessary adsorption time of three metals when using a bio-adsorbent in which red or black tea is completely absent.

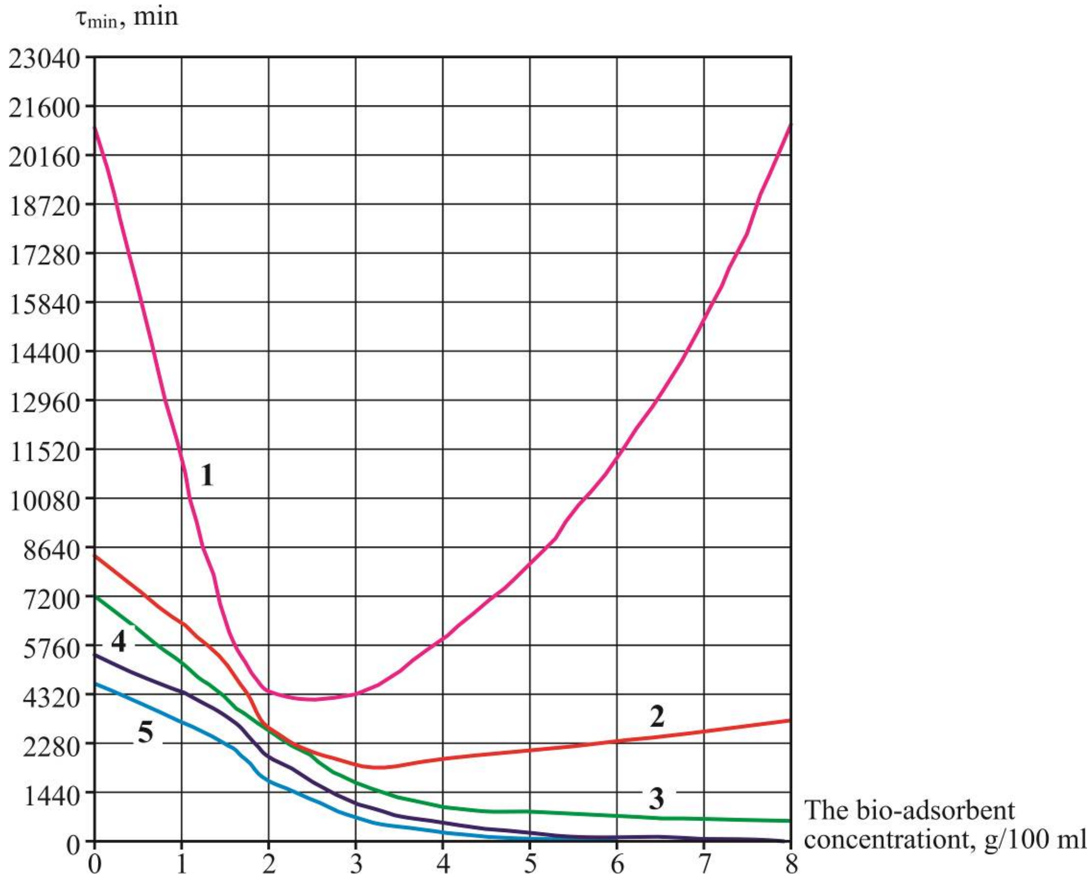


Figure 10. Dependence of the minimum necessary adsorption time of three metals simultaneously before reaching the MPC on the bio-adsorbent composition: 1 – 0% red tea; 2 –5% red tea; 3 – 10% red tea; 4 – 50% red tea; 5 – 100% red tea, T = 25 ± 1 ºC, pH = 3.5

In Figure 10 it is clearly seen that at the red tea absence in the adsorbent (that is, only black tea is used), the adsorption time for all three metals, when they are present simultaneously, is not lower than 4400 min (about 72 hours). If you add 25% of red tea from the total bio-adsorbent dose, the minimum necessary adsorption time of all three metals to the MPC can be reduced to 45 min. If red tea is used (without black tea), the concentration of which is 3%, then complete extraction of Cd, Co and Ni will be achieved in 30 minutes.

5. Conclusions

Based on experimental data, the kinetic regularity of the Cd, Co and Ni adsorption from contaminated water were studied using a bio-adsorbent from red and black tea leaves mixture. In this case, the adsorption regularity were studied both for each metal separately and for all three metals simultaneously. Visual assessment of the kinetic dependency shape showed the presence of at least two parts on the chart, but two parts are very pronounced. The first part of the graph shows a sharp decrease in the concentration of the corresponding metal by 5-10% of the initial value for 1-5 minutes. Thereafter, there is a slower decrease in concentration of metals in contaminated water according to the second part of the graph.

It has been established that red and black tea adsorbs Cd, Co and Ni unequally. The fast process share for Cd decreases with an increase in the red tea amount, and for Co and Ni it increases. However, for all cases, the red tea amount does not exceed 30% of the total bio-adsorbent dose. It was observed that for Cd and Co, an increase in the black and red tea amount leads to a drastic reduction of the adsorption process time (up to 10 times), while for Ni the black tea addition slows down the adsorption process. Therefore, this greatly complicates the implementation of the contaminated water treatment technology from three metals simultaneously on an industrial scale.

Using the adsorption process kinetic regularity, it possible to determine the most rational bio-adsorbent dose and the necessary red and black tea dose in bio-adsorbent to achieve MPC if the initial concentrations of heavy metals are known.

An important technological conclusion was installed: the technological process of Cd, Co and Ni adsorption can be expedient, if it is carried out in several stages with optimal red and black tea amounts for each of the metals. However, adsorption process kinetics study at given initial Cd, Co and Ni concentrations showed, that at the red tea absence in the adsorbent (that is, only black tea is used), the adsorption time for all three metals, when they are present simultaneously, is not lower than 4400 min (about 72 hours). If you add 25% of red tea from the total bio-adsorbent dose, the minimum necessary adsorption time of all three metals can be reduced to 45 min. If red tea is used (without black tea), the concentration of which is 3%, then complete extraction of Ca, Co and Ni will be achieved in 30 minutes. In addition, the proposed statistical generalization of the results of experimental research of the adsorption process can be used to calculate the technological parameters of the process in a wide range of their values.

Acknowledgements

The authors are thankful to Nutrition and Food Sciences Research Center administration, Tehran Medical Sciences, Islamic Azad University (Tehran, Iran) for their support, as well as the administrations all in which the authors of this article work.

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