Research Article

Biosorption of Heavy Metal From Cadmium Rich Aqueous Solutions by Tea Waste as a Low Cost Bio-Adsorbent

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Abstract

Background: Heavy metals pollution is a serious threat to environment and human health. Therefore, it is vital to find an effective method to remove heavy metals from natural resources.

Objectives: The current study aimed to investigate the adsorption capacity of cadmium from synthetic solution by tea waste as a biomass.

Methods: The experiments were conducted in batch system and the effect of pH, adsorbent quantity, contact time and the initial concentration of cadmium were examined. The most common isotherms and kinetics of adsorption were applied to analyze cadmium adsorption and the reaction rate. Moreover, morphological characteristics before and after the adsorption process and also molecular structures of tea waste were determined by scanning electron microscope (SEM) and Fourier transform infrared spectrometry (FTIR); also, the surface area size of tea waste was measured using Brunauer-Emmett-Teller (BET).

Results: According to the results, the maximum efficiency of cadmium adsorption was 99.50% obtained in pH of 5 and contact time of 90 minutes and 10 g/L of adsorbent. With the increase of initial concentration of cadmium, the amount of the adsorbed metal increased, but the removal percentage decreased. Data for this study indicated a good correspondence with both isotherms of Longmire and Freundlich. The analysis of kinetic indicated that cadmium adsorption was consistent with the second-degree kinetic adsorption model.

Conclusions: According to the high efficiency of cadmium elimination by tea waste, this approach is applicable as an efficient and affordable trend to remove cadmium from aqueous solution without any chemical or physical pre-treatment.

Keywords: Cadmium Biosorption, Tea Waste, Kinetic and Isotherm of Adsorption

1. Background

Nowadays, water resources pollution is a great concern caused by heavy metals, radioactive compounds, organic and inorganic substantial. Heavy metals are especially important due to their non-biodegradable nature and harmful physiological effects on animals (1).

One of the main causes of the accumulation of heavy metals in the environment is rapid industrialization and population growth (2). As a result, the effective removal of metals from aqueous environments is considered as an important issue in industrial countries (3, 4). Biochemical toxic effect of heavy metals is due to the strong tendency of metal cations to react with the sulfur. The cations of heavy metals or molecules involve them and enter the body through ingestion, then easily connect to sulfhydryl groups (-SH) abundant in the human body. Metal-sulfur bond usually affects enzymes that control the rate of metabolic reactions in the human body; therefore,

these enzymes cannot do their normal duties and consequently human health falls in danger and sometimes may lead to death (5). Also, cadmium causes damage to liver and lung, blood pressure, kidney failure, birth defects, cancer and mutagen (6). According to potable water standard codified by world health organization (WHO) and the American water works association; the permissible quantity of cadmium in drinking water is 0.005 mg/L (7). There are many methods to remove heavy metal ions from wastewater which can be considered as chemical separation, filtration, membrane separation, electrochemical treatment, adsorption and ion exchange (8). In recent years, adsorption is considered by many environmental friendly researchers due to its simple, low-cost and effective trend to remove heavy metal ions (9-11).

Heavy metals removal by natural and cheap adsorbents was investigated from the 1970s. Larsen and Schierup studied this issue by activated carbon extracted from burning straw to remove cadmium (12). Tarley et al. studied rice

husk to remove metals such as lead while to gain higher efficacy some adjustments were fulfilled ([13]). Ghasemi and Mafigholami succeeded to remove lead from aqueous solutions with high removal efficiency using sawdust of Prosopis (Mimosaceae) ([14]). Cay introduced tea waste as a cheap biosorption to attract copper ([1]). In another research, Hosseini et al. showed that tea waste with magnetite nanoparticles can be an attractive option for heavy metal removal from contaminated water ([15]). Other natural and low cost absorbents such as pine, oak, walnut and natural coagulants can be noted ([16]-[21]). Experimental trials on using natural and inexpensive absorbents are widely applied in various countries to refine industrial wastewater. Adsorption mechanism of heavy metals by tea waste seems to be conducted by compound and groups such as the caffeine, theophylline, tannin, catechin, fluoride, etc. with metals constitute bond and their absorption.

2. Objectives

Statistically, Iran is the 4th largest consumer of tea in the world; therefore it is proposed to deal with feasibility of removing cadmium from aqueous solutions using tea waste which is available in large extent and known as waste. In the current study, the effectiveness of this biomass in the absorption process is discussed.

3. Methods

3.1. The Preparation of Adsorbent

After collection of tea waste adsorbent, it was homogenized by mesh 35 and then it was washed with distilled water to remove dust and other pollutants, then dried in oven at 30°C.

3.2. The Preparation of Synthetic Solutions

Cadmium nitrate was used to make synthetic solution. For this purpose, first the cadmium solution with concentration of 25 mg/L was prepared. Then the other concentrations were prepared by diluting the main solution. All the chemicals were purchased from Merck company (Germany). The experimental stages were conducted at 30°C and the remained concentration of the metal was determined by atomic absorption spectrophotometer (PG model, England) ([22]). It is important to consider that all the experiments were replicated three times and the mean of data and the results were determined and used.

3.3. The Effect of pH on Cadmium Removal

To determine optimum pH, the pH meter (Inolab pH 720 model, Germany), ranging from 3 to 10, was used. After pH adjustment using hydrochloric acid and 0.1 N NaOH solution, considering other fixed parameters, 0.5 g of tea waste was added to 50 mL of the sample with 10 mg/L cadmium concentration. After 30 minutes, the concentration of remained cadmium was measured.

3.4. The Effect of Adsorbent Quantity on Cadmium Removal

In this step, to determine the optimum quantity of adsorbent with consideration of other fixed parameters, 0.15, 0.3 and 0.5 g of tea waste were added to the 50 mL solutions with the initial cadmium concentration of 10 mg/L and with the optimum obtained pH quantity from the previous stage. After 30 minutes of contact time, the concentration of the remained cadmium in the solution was measured.

3.5. The Effect of Contact Time on the Quantity of Cadmium Adsorption

To examine contact time effect with consideration of other fixed parameters, after the preparation of 50 mL solutions with the initial cadmium concentration of 10 mg/L, the optimum quantities of tea waste and pH were exerted to the samples; then they were taken out from the mixer at intervals between 15 to 90 minutes and analyzed.

3.6. The Effect of Initial Concentration of Cadmium on Cadmium Removal

In order to examine the effect of initial concentration of cadmium on the adsorption efficiency, considering initial concentration as variable and the other fixed parameters, 50 mL solutions were prepared with the initial concentrations of 5, 10, 15, 20 and 25 mg/L and analyzed after adjustment and adding the optimum quantity of pH and tea waste in the optimum contact time obtained in the previous stage.

3.7. Morphology, Molecular Structure and Surface Area of Tea Waste

At this stage, scanning electron microscope (SEM) (XL30 model, the Netherlands), Fourier transform infrared spectrometry (FTIR) (PerkinElmer BX-II model, USA) and Brunauer-Emmett-Teller (BET) (Belsorp mini II model, Japan) devices were applied to identify the morphology, molecular structure and surface area of tea waste and cadmium adsorption.

4. Results

4.1. The Examination of pH Effect on Cadmium Removal

Figure 1 shows the results of various pH effects on the adsorption percentage. Based on the achieved results, with the increase of pH up to 5, the removal efficiency increased and decreased after that. According to the conducted studies, in acidic pH, the concentration of H^+ ion is high in the solution and this cation competes with cadmium to set on the adsorption places and cadmium adsorption decreases and in higher pH, concentration of OH^- ion is high and cadmium deposits are observed and adsorption rate decreases. It was consistent with the results of the study by Saki et al., in Iran (6).

4.2. The Effect of Adsorbent Quantity on Cadmium Adsorption Rate

The results of the effect of adsorbent quantity on the cadmium adsorption are presented in Figure 2. The results showed that the removal rate of cadmium by tea waste increased with the increase of adsorbent quantity, since the increase of adsorbent quantity increased the quantity of contact surface of adsorbent with cadmium, the efficiency of adsorption increased. These results were consistent with those of the study by Kumar et al. titled: "Removal of copper from aqueous solution using *Ulva fasciata* sp., a marine green algae", in India (23); also consistent with the results of the study by Ozer et al. (24).

4.3. The Effect of Contact Time on the Adsorption Rate of Cadmium

The results of different contact time on the adsorption rate of cadmium are shown in Figure 3. Based on the results, removal efficiency increased parallel with the increase of contact time and after 90 minutes, it reached maximum removal level and this time was considered as
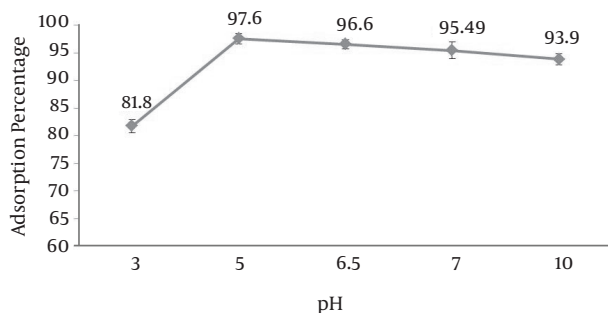

Figure 2. Effect of Different Adsorbent Quantity on Adsorption rate of Cadmium (pH = 5, Contact Time = 30 Minutes, Initial Concentration of Cadmium = 10 mg/L)

the equilibrium response time. The reason for this behavior was that with the increase contact time, encounter between adsorbent and metals increased. It was consistent with the results of the study by Chonjnaka et al. titled: "Biosorption of Cr 3+, Cd 2+ and Cu 2+ ions by blue-green algae *Spirulina* sp.; kinetics, equilibrium and the mechanism of the process", in Poland (25).

4.4. The Effect of Initial Concentration of Cadmium on the Removal Percentage and Adsorption Capacity of Cadmium

The quantity of adsorbed substance (adsorption capacity) is defined as follows (14):

$$q_e = (C_0 - C_e) \times \frac{V}{W} \tag{1}$$

Where C_0 is the initial concentration of adsorbed substance (mg/L), C_e is the concentration of the adsorbed substance after adsorption (mg/L), V is the volume of the solution (L) and W is the weight of adsorbent substance (g).

The results of examination of the initial concentration effect of cadmium on adsorption are shown in Figure 4. The data showed that with the increase of initial concentration of cadmium, the quantity of adsorbed substance (adsorption capacity) increased, but the adsorption percentage decreased, in a way that with the increase of initial con-

Figure 1. Effect of Various pH Levels on the Adsorption Rate of Cadmium (Adsorbent Quantity = 10 g/L, Contact Time = 30 Minutes, Initial Concentration of Cadmium = 10 mg/L)
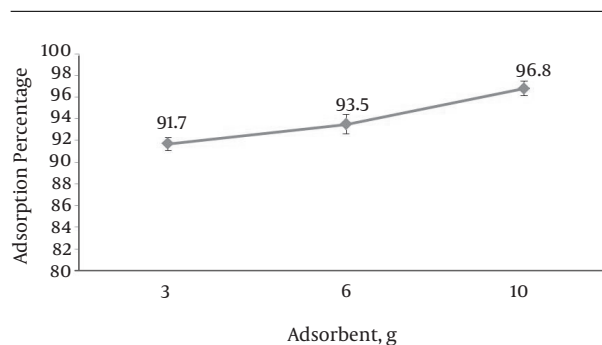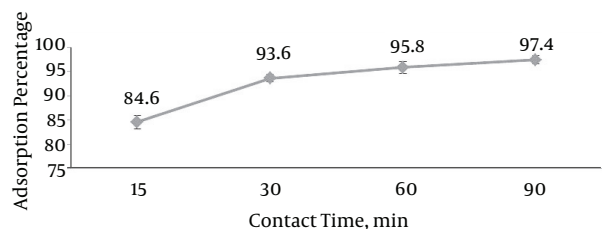

Figure 3. Effect of Different Contact Times on the Adsorption Rate of Cadmium (pH = 5, Adsorbent Quantity = 10 g/L, Initial Concentration of Cadmium = 10 mg/L)

centration of cadmium from 5 to 25 mg/L, adsorption capacity increased from 0.497 to 2.397 mg/g and removal percentage decreased from 99.5% to 95.88%. This issue can be concluded due to more free bands of adsorbent and ion exchange in low concentrations of cadmium. Furthermore, in batch adsorption systems, the input concentration of cadmium in the solution plays a crucial role as the motivating force to overcome the resistance of the mass transfer between liquid and solid phases. Therefore, with the increase of cadmium concentration in the solution, the adsorption capacity of cadmium increased. These results were consistent with those of the study by Saki et al. conducted in Iran (6).

4.5. Isotherms Studies of Cadmium Adsorption by Tea Waste

Analytical information was obtained from isotherms to develop necessary equation for designing. Furthermore, adsorption isotherm can be used to describe the reaction of adsorbing substance with adsorbent and optimize the quantity of adsorbent application (26).

4.5.1. Langmuir Isotherm

The linear form of Langmuir equation is as follows (6, 27, 28):

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m \times K_1 \times C_e} \tag{2}$$

Where q_e is the amount of adsorbed substance (mg/g), q_m and K_1 are Langmuir parameters related to the maximum adsorption capacity and the correlation energy of adsorption respectively. The quantities of q_m and K_1 can be determined by drawing the changes of $1/q_e$ based on $1/C_e$. The main characteristic of Langmuir equation is a dimensionless constant called equilibrium parameter defined as follows (29):

$$R_L = \frac{1}{1 + K_1 \times C_0} \tag{3}$$

R_L indicates the type of isotherm. $0 < R_L < 1$ for optimum adsorption, $R_L > 1$ for non-optimum adsorption, $R_L = 1$ for linear adsorption and $R_L = 0$ for irreversible adsorption (30). The results of Langmuir isotherm analyses are shown in Table 1, according to the obtained results of $R_L = 0.0025$ and correlation coefficient of $R^2 = 0.9317$, achieved data were conformed to Langmuir isotherm.

4.5.2. Freundlich Isotherm

The linear form of Freundlich equation is as follows (31-33):

$$Logq_e = LogK_F + \frac{1}{n}LogC_e \tag{4}$$

Where K_F is adsorption capacity (mg/g), $1/n$ is the intensity of adsorption, C_e is the equilibrium concentration (mg/L) and q_e is the adsorbed substance (mg/g). From the linear diagram $\log(q_e)$ against $\log(C_e)$, K_F and $1/n$ are determined that $1/n$ indicates the type of adsorption process, if $1/n = 0$ it shows irreversible process, $0 < 1/n < 1$ shows optimum adsorption state and if $1/n > 1$ indicates non-optimum adsorption (34). The results of Freundlich isotherm analyses are shown in Table 2, according to the obtained results of $1/n = 0.409$ and correlation coefficient of $R^2 = 0.9791$, achieved data were conformed to Freundlich isotherm. Of course it is necessary to consider that conforming the adsorption process by Langmuir isotherm does not mean that compliance of all the Langmuir hypotheses and formulating Langmuir are rarely compatible in a wide range of the concentrations, while the Freundlich isotherm is more sufficient and completely compliance to data. These results were consistent with those of the study by Hosseeini et al. titled: "Removal of Cu (II) from aqueous solution by modified tea waste with magnetic nanoparticles", in Iran (15).

4.6. Kinetic Studies of Cadmium Adsorption by Tea Waste

One of the most important factors of adsorption process is prediction of adsorption rate. The adsorption kinetic depends on the physical and chemical properties of adsorbent that affects adsorption mechanism.

#### 4.6.1. The Kinetic Model of the First-Degree Adsorption

The first-degree adsorption kinetic can be described as follows (35-37):

$$Log(q_e - q_t) = Logq_e - \frac{K_1}{2.0303}t \tag{5}$$

In this equation, q_e is the adsorption capacity of tea waste in equilibrium condition (mg/g), q_t is the quantity of adsorbed cadmium in time (mg/g) and K_1 is a constant of first-degree equilibrium velocity (1/min). The first-degree kinetic model is obtained by linear drawing of $\log(q_e-q_t)$ on the basis of t, which K_1 and q_e are drawn from slope and intercept, and R^2 correlation coefficient can be also obtained from the diagram. The results of the first-degree adsorption kinetic are shown in Table 3. According to the parameters and diagram, it can be concluded that the data do not follow the first-degree adsorption kinetic model, since in spite of optimum R^2, quantities of q_e from the experiment are not equal to those of the diagram.

4.6.2. The Kinetic Model of the Second-Degree Adsorption

The second-degree adsorption kinetic model is also one of the most common models to analyze the kinetic of adsorption reactions is as follows (38, 39):
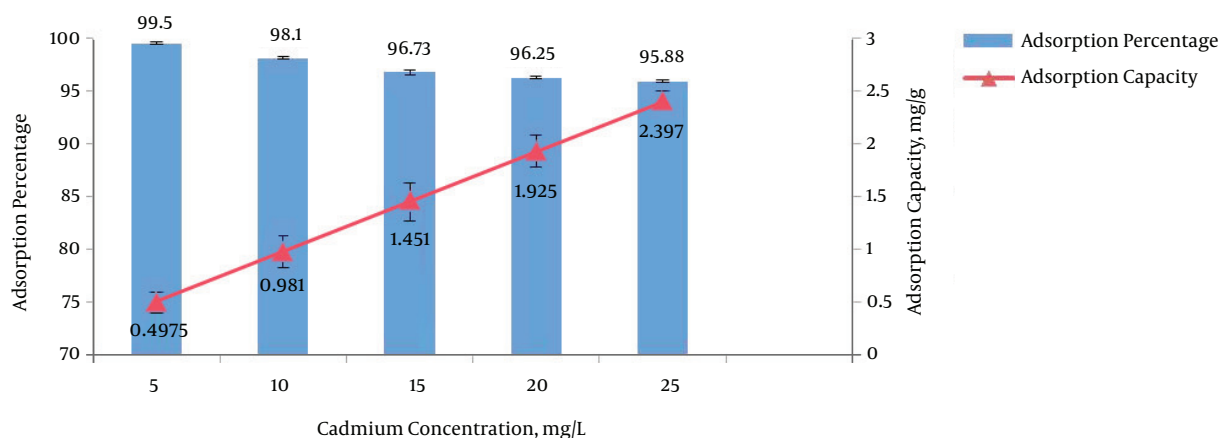
Figure 4. Effect of the Quantity of Different Initial Concentration on the Capacity and Percentage of Cadmium (pH = 5, Adsorbent Quantity = 10 g/L, Contact Time = 90 Minutes)

Table 1. Results of Langmuir Isotherm Calculations

Equation Line	q_m	K_l	R_L	R^2
Y = 0.0368x + 0.5656	1.76	15.36	0.0025	0.9317

Table 2. Results of Freundlich Isotherm Calculations

Equation Line	K_F	1/n	R^2
Y = 0.4099x + 0.3279	1.2.127	0.409	0.9791

$$\frac{1}{q_t} = \left[\frac{1}{q_e}\right] t + \left[\frac{1}{K_2 \times q_e^2}\right] \quad\quad (6)$$

In which, q_e is the adsorption capacity of tea waste in the equilibrium condition (mg/g), q_t is the adsorbed cadmium quantity in time (mg/g) and K_2 is a constant of second-degree equilibrium velocity (g/mg/min). The second-degree kinetic model is obtained by linear drawing of t/q_t on the basis of t that q_e and K_2 are drawn from slope and intercept and correlation coefficient R^2 can be also obtained from the diagram. The results of the second-degree adsorption kinetic are shown in Table 4. According to the parameters and diagram, it can be concluded that the data follow the second-degree adsorption kinetic model since the quantity of R^2 is optimum and obtained q_e quantities from the experiment are equal to those of the diagram. The study by Chen et al. to determine the kinetic behavior of adsorption heavy metals in China clarified that the adsorption of heavy metals in aqueous solutions was consistent with the second-degree kinetic adsorption model (40).

4.7. Morphological Study and Surface Area of Tea Waste

Figures 5 and 6 show images from the surface structure of tea waste by scanning electron microscope (SEM). Figure 5 shows the images before the adsorption of tea waste in different magnifications that show porous structure. Figure 6 shows the images after the adsorption of tea waste in different magnifications that metals have filled pores and the adsorption process is also conducted according to the results of the BET analysis, surface area of tea waste was 0.79 m²/g.

4.8. Identifying the Molecular Structure of Tea Waste Compounds

In Figure 7, given the obtained frequencies which are 1500 - 4000 cm⁻¹, it is indicated that there are O-H, C-H, C = C and C = N bonds and cell walls generally contain caffeine, theophylline, tannin, catechin, fluoride, etc.

5. Discussion

The results of the study indicated that the highest adsorption efficiency was 99.50% achieved in optimum conditions of pH = 5, adsorbent quantity of 10 g/L, 90 minutes of contact time and the initial cadmium concentration of 5 mg/L. With the increase of initial concentration of cadmium, the amount of the adsorbed metal increased, but the removal percentage decreased. The study data indicated a good correspondence with both isotherms of

Table 3. Kinetic Results of the First-Degree Adsorption

Equation Line	K_1	q_e (Calculated)	q_e (Experiment)	R^2
Y = -0.019x - 0.705	0.038	0.197	0.974	0.92

Table 4. Kinetic Results of the Second-Degree Adsorption

Equation Line	K_1	q_e (Calculated)	q_e (Experiment)	R^2
Y = 1.0009x + 2.4409	0.410	0.999	0.974	0.9997
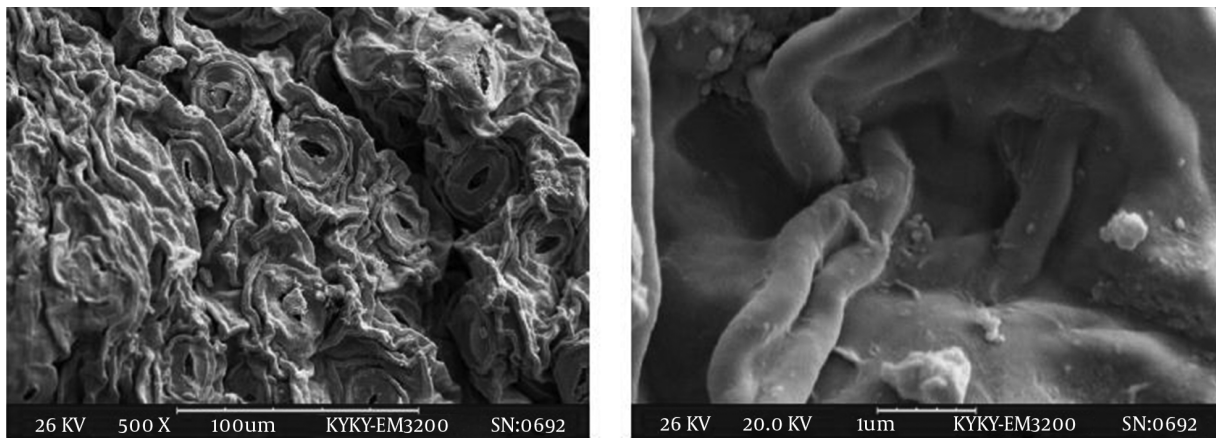
Figure 5. SEM Images Before Adsorption of Metal by Tea Waste; 500 X and 20 KX Magnifications
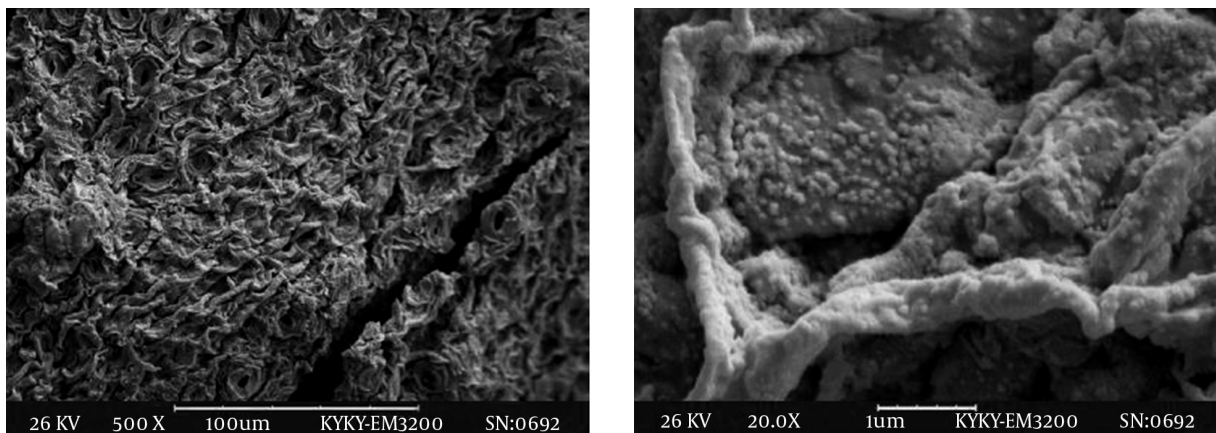
Figure 6. SEM Images After Adsorption of Metal by Tea Waste; 500 X and 20 KX Magnifications

Longmire and Freundlich. The analysis of kinetic indicated that cadmium adsorption was consistent with that of the second-degree kinetic adsorption model. According to the considerable removal percentage of tea waste in cadmium removal, this method can be considered as an effective method to remove heavy metals. Complex structure in cell wall of the absorbents led to a variety of mechanisms in regard to charge trapping metal ions subpoenaed. Ion exchange and formation of hydrogen bonds are among the principles of mechanisms for biosorption of metal ions (41).
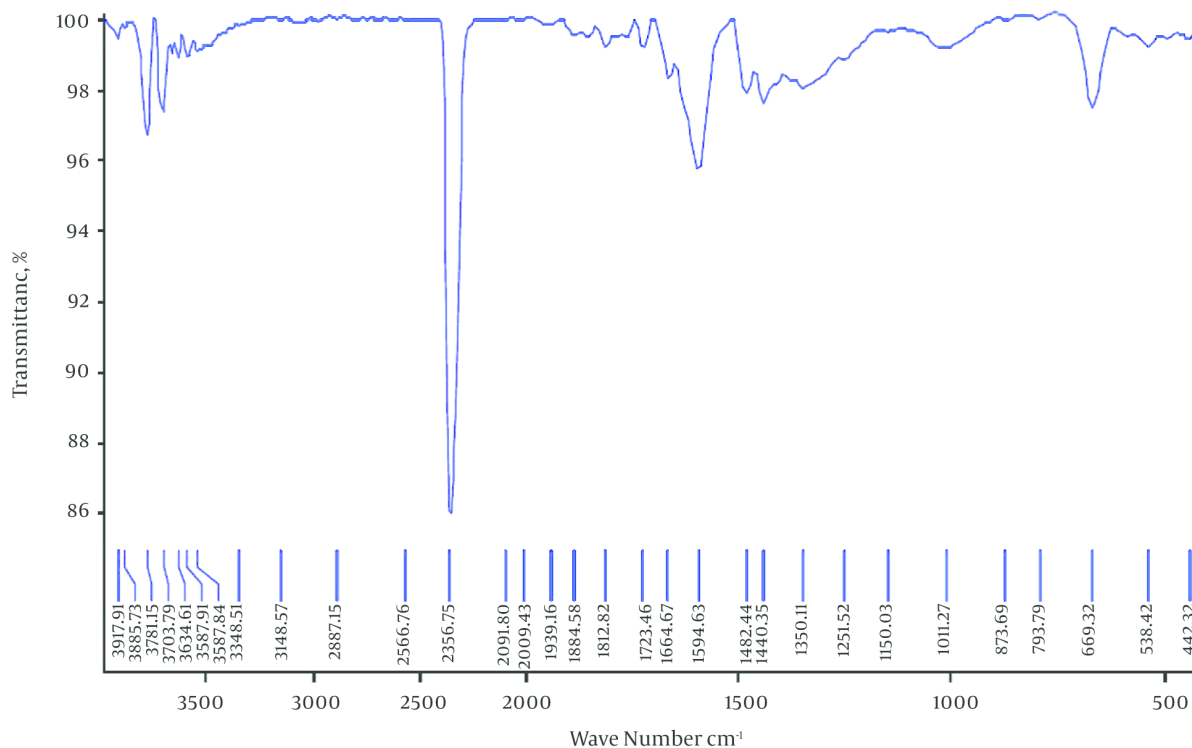
Figure 7. Tea Waste Analysis by FTIR

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Footnote

Authors' Contribution: Study concept and design: Roya Mafi Gholami; analysis and interpretation of data: Sadegh Ghasemi and Mohsen Yazdanian; drafting of the manuscript: Sadegh Ghasemi and Mohsen Yazdanian; critical revision of the manuscript for important intellectual content: Roya Mafi Gholami and Sadegh Ghasemi; statistical analysis: Sadegh Ghasemi and Mohsen Yazdanian

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