

# Single and competitive adsorption of $\text{Cu}^{2+}$ and $\text{Pb}^{2+}$ by tea pulp from aqueous solutions

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## Abstract

**Background:** Removal of heavy metals by bioadsorbents is one of the effective and inexpensive methods for water and wastewater treatment. The aim of this study was to investigate the ability of tea pulp in order to remove  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  metals in two states of adsorption (single element and two elements) from aqueous solutions.

**Methods:** Experiments were performed on synthetic and real samples at ambient temperature. The effect of solution pH, adsorbent dose, contact time, and initial concentration on single and competitive removal of copper metals and lead was studied. Adsorption kinetics and adsorption isotherms were analyzed by *pseudo*-second-order kinetic equations, Elovich model and intraparticle diffusion, Freundlich and Langmuir equations, respectively.

**Results:** The maximum adsorption capacity for copper and lead was observed at pH = 5-8 and pH = 4-8, respectively. Maximum adsorption capacity for copper and lead by tea pulp in single-element solution (single) was 37.17 and 48.54 mg/g and in two-element solution (competitive), was 28.41 and 43.47 mg/g, respectively. The adsorption reaction of heavy metals by tea pulp followed the Langmuir isotherm and *pseudo*-second-order kinetic models.

**Conclusion:** Tea pulp as an inexpensive bioadsorbents is able to remove about one-third of the copper, and approximately, half of lead from aqueous solutions, so its use in the treatment of aqueous solutions will be beneficial.

**Keywords:** Copper, Lead, Adsorption, Tea

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## Introduction

Heavy metals are one of the most important environmental concerns due to toxicity, stability, accumulation, and transport in the food chain. These pollutants enter water, soil, and air through natural processes (such as physical erosion, chemical degradation, etc.) and often through human resources (1). Industrial processes seriously release toxic heavy metals into water streams. Mining activities, plating and processing of metals, textile production, production of insecticides, pesticides and battery production are the main sources of water pollution by heavy metals. Lead, cadmium, copper, arsenic, chromium, zinc, and mercury are known as heavy metals (2).

Heavy metal toxicity can reduce mental activity and cause dysfunction of the central nervous system. Low energy levels and damage to the composition of the blood, lungs, kidneys, liver and other vital organs are other side effects of heavy metals entering the body. The presence of metals in water currents and seawater poses a threat to the

health of aquatic communities, especially fish (2, 3). As a result, many countries have strict and restrictive laws to control water pollution. According to the standard of the US Environmental Protection Agency (EPA), the standard and acceptable limits of copper and lead in drinking water are 1.3 and 0.015 mg/L, respectively (4).

Removal of heavy metal ions from wastewater is an effective method to reduce environmental pollution and water treatment and various methods have been proposed to remove heavy metal pollution. Traditional methods of removing pollution from liquid and gaseous phases include biological treatment, coagulation (5), membrane separation processes, chemical sediment, ion exchange (6), advanced oxidation (7-9) and adsorption using adsorbents (10, 11). Among these methods, adsorption has been recognized as an effective and cost-effective method for removing many water contaminants (4).

Among adsorbents, adsorption by activated carbon is an effective and safe method; activated carbon has



some advantages such as high surface area, fine porous structure, uniform distribution of pore size, high porosity, high surface reactivity, high mechanical strength and strong adsorption capacity (12-14), but the high cost of using activated carbon method has forced researchers to study cheaper methods to replace this method. One of the alternative methods is the use of produced wastes in agriculture and plant wastes. Agricultural waste has a weak and porous structure and includes active groups of carboxyl, hydroxyl and other reactive groups that can be effective for the surface adsorption of contaminants (15).

The agricultural wastes used for adsorption and removal of heavy metal contaminants include rice straw (16), banana peel (17), walnut shell (18), olive-mill waste (19), mustard plant ash (20,21), cucumber peel (22,23), and tea waste (24,25). Tea is one of the most popular drinks and in fact, about three and a half million tons of tea are consumed worldwide each year. About 120 000 tons of world consumption belong to Iran. This volume of tea consumption will produce a lot of tea pulp that enters the environment through daily consumption of tea (25).

Waste from daily tea consumption can be used as an inexpensive adsorbent to remove and adsorb heavy metals from aqueous solutions. The intensity of adsorption and the amount of adsorption of metal ions by tea pulp and other organic wastes depend on the physical and surface properties of the adsorbent, the properties of the metal ion, and the adsorption conditions.

As so far no research has been done on the ability of tea pulp to adsorb the two elements of copper, especially in a competitive situation (copper and lead), this study was conducted to investigate the ability of Iranian tea pulp to remove copper and lead metal ions from aqueous solutions in single (single element) and competitive (two elements) in synthetic and real solutions as a cheap and available bioadsorbent.

## Materials and Methods

### Materials

All chemicals, including  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{PbCl}_2$ ,  $\text{HCl}$ , and  $\text{NaOH}$  were analytical-grade reagents from Merck (Germany). In this study, tea wastes of black tea were used for the experiments.

### Preparation of adsorbent

The soluble and colored compounds of the tea wastes of black tea were washed several times with boiling water to make the resulting solution completely colorless. Then, the tea wastes were washed with distilled water and dried in oven at  $60^\circ\text{C}$  for 24 hours. The dried tea wastes were milled and passed through a 0.5-mm sieve to prepare for adsorption tests (26).

### Characterization techniques of tea wastes

Scanning electron microscopy (SEM) was used to

determine the surface morphology of the tea pulp (11).

### Batch sorption studies for heavy metals removal

This experimental research was completed in winter 2021 at the Environmental Health Engineering Research Center of Kerman University of Medical Sciences. Adsorption studies were performed to investigate the effect of various parameters such as contact time (45 and 90 minutes), pH (2-8), initial concentration of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  (100-500 mg/L), and adsorbent concentration (2, 4, 6 g).

For this purpose, stock solutions of copper and lead (1000 mg/L) were prepared by dissolving the appropriate amount of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{PbCl}_2$  in distilled water. The wastewater (real sample) used in this study was collected from the effluent of Shahid Bahonar Copper Complex in Kerman (Copper) and Battery Industries located in Kerman Industrial Town 2. Batch experiments were performed to investigate the effect of various parameters on copper and lead removal. Adsorption experiments were performed in a 50-mL polyethylene test tube containing 25 mL of the solution. The tubes were shaken in a horizontal flat shaker at 120 rpm for a specified time (24 hours). The test tube was shaken in a horizontal flat shaker at 120 rpm for a specified time (24 hours). At the end of the experiment, the adsorbents were removed from the suspension by centrifugation at 5000 rpm (20 minutes) and the solutions were filtered through filter paper.  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  concentrations were measured by an atomic absorption spectrophotometer (SpectrAA-774-Varian model) ( $\text{Pb}$ :  $\lambda = 240.7$  nm,  $\text{Cu}$ :  $\lambda = 324.7$  nm) (25, 26). All adsorption experiments were performed in three replicates.

The adsorption capacity adsorbent ( $q_e$ ) and the removal efficiency ( $R$ ) were calculated using equations (1) and (2):

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

$$R = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)$$

Where  $q_e$  (mg/g) is the adsorption capacity of adsorbent,  $C_0$  (mg/L) is the initial concentration heavy metals,  $C_e$  (mg/L) is the equilibrium concentration of metal ions,  $V$  (L) is the volume of metal ions solution, and  $m$  (g) is the weight of the sorbent.

### Adsorption isotherms

Experiments of adsorption isotherms were performed by  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  solutions at different initial heavy metal concentrations (0, 5, 25, 50, 100, 200, 300, 400, and 500 mg/L) at  $25^\circ\text{C}$  and 4 g/L of tea waste. In single-element mode,  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  concentrations were used separately and in the competitive adsorption mode (two elements),  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  concentrations were used. With the help of adsorption isotherms, the ability to adsorb different

adsorbents can be detected. In this study, the adsorption isotherms of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  were described numerically using the parameters obtained from the Freundlich and Langmuir equations 3 and 4:

$$\text{Log}q_e = \text{Log}k_f + \frac{1}{n} \text{Log}C_e \quad (3)$$

$$\frac{C_e}{q_e} = \frac{1}{Mk_L} + \frac{C_e}{M} \quad (4)$$

where  $q_e$  (mg/g) and  $C_e$  (mg/L) are adsorption capacity and equilibrium concentration, respectively,  $M$  (mg/g) is the maximum adsorption capacity of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  on the surface of adsorbent,  $K_L$  (L/mg) is the rate of adsorption (Langmuir constant),  $K_f$  and  $n$  are Freundlich constants,  $K_f$  is adsorption capacity [(mg/g) (L/mg)  $1/n$ ], and  $n$  is the tendency to adsorb. Freundlich model can be used for non-ideal adsorption on heterogeneous surfaces and multilayer adsorption. The Langmuir model assumes that adsorption occurs at specific homogeneous surfaces and there is no interaction between the adsorbed molecules (25).

#### Adsorption kinetics

The effect of contact time on the adsorption of heavy metals by adsorbents at different times of 5 to 720 minutes at 25°C was investigated. The initial concentration of heavy metals was 100 mg/L and the adsorbent was 2, 4, and 6 g/L. The adsorption kinetics of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  were analyzed by pseudo-second-order kinetic, intraparticle diffusion and Elovich equations (5,6,12):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

$$q_t = k_p t^{\frac{1}{2}} + C \quad (6)$$

$$q_t = a + b \ln t \quad (7)$$

Where  $q_e$  is the capacity of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  adsorbed on the tea waste surface at equilibrium (mg/g),  $q_t$  is the capacity of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  adsorbed on the tea waste surface at time  $t$  (mg/g),  $K_2$  is the constants of the equilibrium rate of first- and second-order kinetics (1/h), and  $t$  is the adsorption time (h),  $K_p$  is the constants of the intraparticle diffusion rate (mg (min<sup>1/2</sup> · g)<sup>-1</sup>),  $C$  is the y-intercept that is related to the thickness of the boundary layer,  $a$  is the rate of initial adsorption (mg (g · min)<sup>-1</sup>), and  $b$  is related to the amount of surface coverage and activation energy (g mg<sup>-1</sup>) (26).

#### Real solution

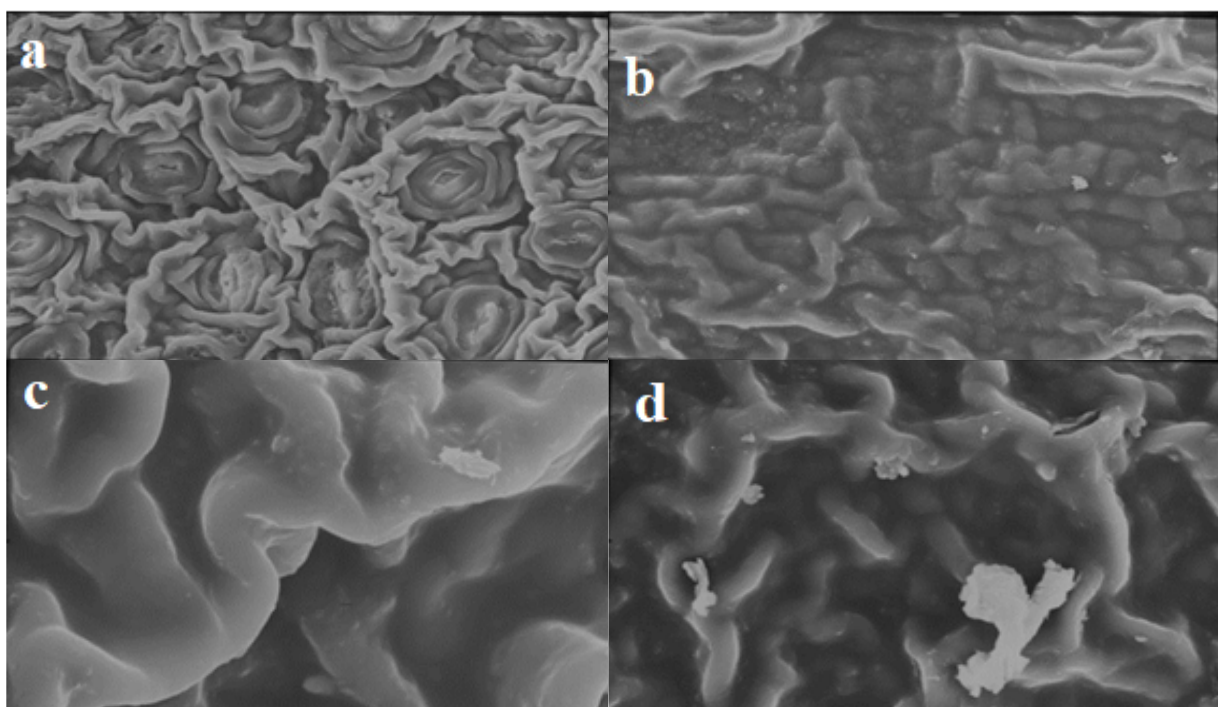
In this research, adsorption tests were performed using synthetic solutions. After determining optimal conditions, tests were done on wastewater from the effluent of Shahid Bahonar Copper Complex in Kerman (Copper) and Battery Industries located in Kerman Industrial Town 2.

#### Results

##### Characterization of tea pulp

##### SEM test

The SEM images below show the morphology of the tea pulp and the adsorption of heavy metals by the bioadsorbent. Figure 1 shows tea pulp before use as a



**Figure 1.** Tea pulp before use as a bioadsorbent (a), Tea pulp after use as a bioadsorbent in copper solution (b), Tea pulp after use as a bioadsorbent in lead solution (c), and Tea pulp after use as a bioadsorbent in a competitive copper and lead solution (d).

bioadsorbent (a), tea pulp after use as a bioadsorbent in copper solution (b), tea pulp after use as a bioadsorbent in lead solution (c), and tea pulp after use as a bioadsorbent in a competitive copper and lead solution (d).

As shown in Figure 1, the adsorption of heavy metals copper and lead is clearly evident by the tea pulp.

### Effect of pH solution on removal efficiency

The effect of pH was studied in the range of 2 to 8 at 25°C. The pH of the solution was adjusted using 0.1 M sodium hydroxide or 0.1 M hydrochloric acid to reach the desired pH. The results of the effect of pH on the adsorption of copper and lead metals by tea pulp in synthetic samples are shown in Figure 2.

Copper and lead removal efficiency at pH=2, was 22% and 40%, respectively. By increasing pH, the removal efficiency of both metals also increased and the maximum adsorption of copper and lead occurred at pH=5 and 4, respectively. Then, the removal of copper and lead remained stable until the pH of 8% and did not change.

### Effect of contact time on removal efficiency

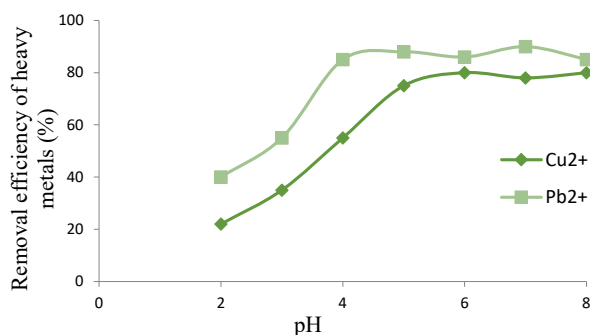
The results of the effect of contact time on the removal efficiency of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  by tea pulp are shown in Figure 3.

Adsorption of copper and lead by tea pulp increased to 45 and 30 minutes, respectively. Further increase in contact time had no effect on increasing the adsorption of both elements, and equilibrium was achieved in less than one hour. Therefore, both elements were adsorbed by tea pulp in a short time and their adsorption process occurred quickly.

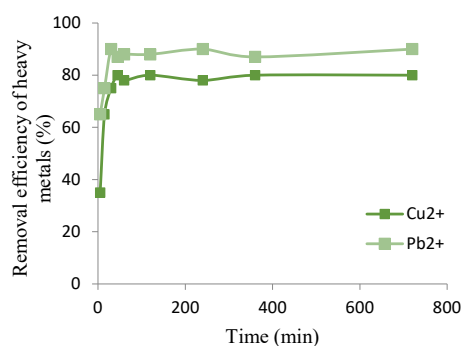
### Effect of initial and equilibrium $\text{Cu}^{2+}$ and $\text{Pb}^{2+}$ concentration on removal efficiency and adsorption capacity

The results of the initial and equilibrium  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  concentration on the removal efficiency and adsorption capacity of adsorbent from aqueous solutions in both single and competitive states are shown in Figure 4a and b, respectively.

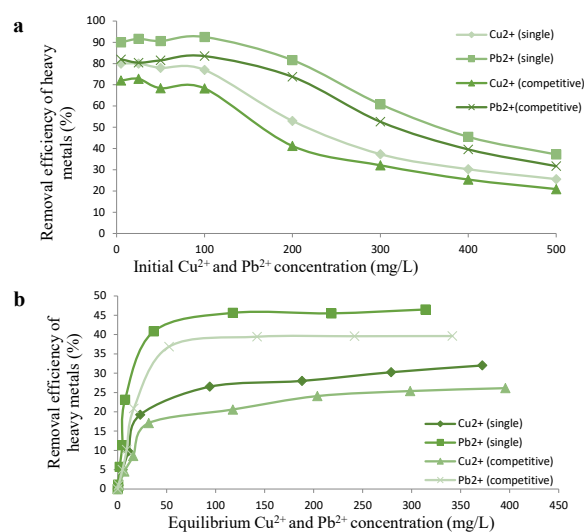
Removal efficiency of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  in the single



**Figure 2.** The effect of pH on removal of copper and lead by tea pulp in synthetic samples.



**Figure 3.** Effect of contact time on removal efficiency of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  from aqueous solutions.



**Figure 4.** Effect of initial and equilibrium  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  concentration on removal efficiency (a) and adsorption capacity (b) in both single and competitive adsorption modes.

adsorption state was decreased by 80% to 25.60% and 90% to 37.20%, respectively. Also, removal efficiency of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  in the competitive adsorption state was decreased from 72% to 20.90% and from 82% to 31.70%, respectively. Removal efficiency was decreased when the initial  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  concentrations were increased, due to the saturation of the exchange sites by adsorption. Therefore, the removal efficiency of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  in the competitive state was lower than that in the single state. The removal efficiency of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  in the single and competitive adsorption states were:  $\text{Cu}^{2+}$  (competitive adsorption) <  $\text{Cu}^{2+}$  (single adsorption) <  $\text{Pb}^{2+}$  (competitive adsorption) <  $\text{Pb}^{2+}$  (single adsorption). Thus, in the competitive state, the removal efficiency of both heavy metals was lower than the single state. Also, removal efficiency of  $\text{Cu}^{2+}$  was lower than that of  $\text{Pb}^{2+}$  in both single and competitive states.

### Effect of adsorbent dosage on removal efficiency

The rate of removal of heavy metals in different amounts of adsorbent at equilibrium contact time in synthetic and real samples is presented in Table 1.

The amount of lead adsorption by the adsorbent in the synthetic and real solution is shown in Figure 5.

The results show that with increasing the amount of adsorbent, the percentage of metal removal in both solutions increased. The percentage of metal removal in the synthetic solution was higher than that in the real solution. For example, in the amount of adsorbent 2 g, the percentage of lead removal in real and synthetic solution was 63.8% and 86.1%, respectively. Also, the percentage of copper removal in the amount of adsorbent 2 g in real and synthetic solution was 57.9% and 82.3%, respectively. At higher adsorbent values, the difference between the percentage of removal of real and synthetic solution was smaller. The presence of ions and impurities in the real solution probably competes to occupy the adsorbent sites, thus, reducing the adsorption compared to the synthetic conditions.

### Adsorption isotherm

In this study, the Langmuir and Freundlich equations were used to investigate the adsorption process of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  as shown in Figure 6a and 6b, respectively.

The parameters of the Langmuir and Freundlich equations for describing  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  adsorption in both single and competitive states are presented in Table 2.

The results presented in Table 2 show that the Langmuir equation describes the adsorption of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  by tea waste better than the Freundlich equation (Langmuir  $R^2=0.99$  and Freundlich  $R^2=0.84-0.89$ ). The higher Langmuir  $R^2$  indicated that the adsorption of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  was monolayer adsorption. The maximum single layer adsorption capacity of the Langmuir equation ( $M$ )

for  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  metals in the single adsorption state, was 37.17 and 48.54 mg/g while in competitive adsorption state, was 28.41 and 43.47 mg/g, respectively. Therefore, the maximal adsorption capacity of the Langmuir equation was close to the experimental data.

### Adsorption kinetic

In order to predict the kinetic mechanisms of the adsorption process, the pseudo-second-order, the intraparticle diffusion and Elovich models were investigated for  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  adsorption as shown in Figure 7a, 7b, and 7c, respectively.

The best fitted model was selected based on the proportion between the experimental and theoretical values and the coefficient of explanation. The results of all three models showed that Elovich models and intraparticle diffusion are not able to predict experimental kinetic data over time due to relatively low values of the coefficient of explanation. But the pseudo-second-order model showed a high coefficient of explanation, so for both heavy metals, the pseudo-second-order model explains the kinetic processes better than the other models. The parameters of kinetic models for adsorption of copper and lead by tea pulp are presented in Table 3.

### Removal of $\text{Cu}^{2+}$ and $\text{Pb}^{2+}$ from real wastewater by tea pulp

The physicochemical properties of raw wastewater sample from copper and battery industries are shown in Table 4.

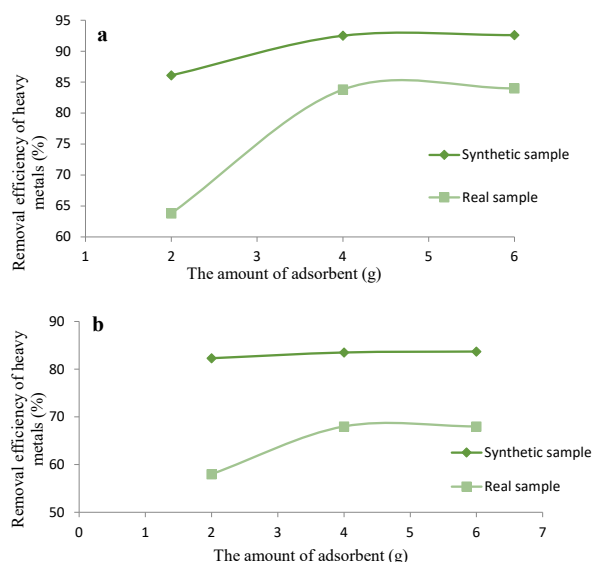
### Comparison of the study results with the results of other studies

**Table 1.** Heavy metal removal rate in different amounts of adsorbent during equilibrium contact

Heavy Metal	Adsorbent Contact Time (min)		Adsorbent Amount (g)		Final Metal Concentration in Synthetic Samples		Adsorption Rate (mg/g)	
	Synthetic Solution (Initial Concentration of 100 mg/L)	Real Solution	Synthetic Solution (Initial Concentration of 100 mg/L)	Real Solution	Synthetic Solution (Initial Concentration of 100 mg/L)	Real Solution	Synthetic Solution (Initial Concentration of 100 mg/L)	Real Solution
$\text{Pb}^{2+}$	90	90	2	2	13.9	19.9	21.5	8.7
$\text{Cu}^{2+}$	45	45	2	2	17.7	2.2	21.05	0.1
$\text{Pb}^{2+}$	90	90	4	4	7.5	8.9	23.1	11.5
$\text{Cu}^{2+}$	45	45	4	4	16.5	1.7	20.9	0.23
$\text{Pb}^{2+}$	90	90	6	6	7.4	8.7	7.7	11.6
$\text{Cu}^{2+}$	45	45	6	6	16.3	1.7	6.9	0.7

**Table 2.** Parameters of the Langmuir and Freundlich adsorption isotherm models for adsorption of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  by tea waste in both single and competitive states

Adsorption Type	Heavy Metals	Langmuir Parameters			Freundlich Parameters		
		$R^2$	$k_L$ ( $\text{L}\cdot\text{mg}^{-1}$ )	$M$ ( $\text{mg}\cdot\text{g}^{-1}$ )	$R^2$	$1/n$	$k_F$
Single adsorption state	$\text{Cu}^{2+}$	0.99	0.033	37.17	0.88	0.53	1.87
	$\text{Pb}^{2+}$	0.99	0.076	48.54	0.84	0.52	3.71
Competitive adsorption state	$\text{Cu}^{2+}$	0.99	0.028	28.41	0.89	0.59	1.34
	$\text{Pb}^{2+}$	0.99	0.039	43.47	0.87	0.59	2.04



**Figure 5.** Percentage of lead removal (a) and copper removal (b) in synthetic and real solution.

Table 5 shows a comparative evaluation of the Pb (II) and Cu (II) measured in this study with the results of other studies.

### Discussion

In soluble systems, the adsorption capacity of metals depends on the pH of the solution, which will be determined by the ratio of hydrogen ions to hydroxyl (31). Factor groups of adsorbent and the adsorbed (heavy metal, color) can be protonated or deprotonated to produce a surface charge. The production of these different surface charges in solution depends on the pH changes (32). In general, the removal of cationic metals or alkaline dyes increases when the pH of the solution increases, while the removal of anionic metals or acidic dyes decreases. In some cases, higher pH level causes the deposition of cationic metals, and in these cases, it is necessary to neutralize the pH (31).

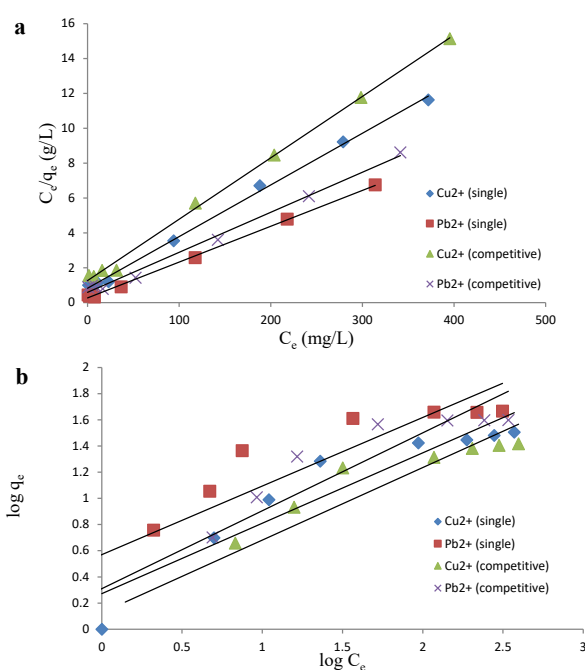
The findings of the present study showed changes in the uptake of copper and lead at different pHs. When the pH is quite low (about 2), there are hydrogen ions in the aqueous solution that compete with metal ions for adsorption on adsorption sites. As a result, the adsorption of copper and lead metal ions at pH 2 is quite low (33). But as the pH of the solution increases, the number of hydrogen ions in the solution begins to decrease. Thus, copper ions have a greater chance of occupying adsorption active sites (33). In this study, the maximum adsorption was observed when the pH of the solution for copper and lead reached 5 and 4, respectively.

Then, at higher pH levels to 8, the amount of copper and lead adsorption remained constant. In a study by Wu et al in Taiwan, the ability of coffee powder to remove lead and zinc from aqueous solutions was investigated. The results showed that maximum removal of lead and zinc from the

solution occurred at pH 5 (34). In a study by Weng et al in Taiwan, the ability to remove copper by treated black tea was examined. They also noted that at pHs above 7, there is a possibility of copper precipitation in the form of copper hydroxide (26).

At pHs above 7, the removal process is the result of both adsorption and deposition processes. In a study by Mazaheri-Tehrani et al in Iran, it was shown that the optimal pH of adsorption is 4.5 and with decreasing or increasing the pH, the adsorption capacity decreases (24). The study of Amarasinghe and Williams in India also showed that the maximum adsorption of copper and lead by tea pulp occurs at the pH range of 5-7 and the minimum adsorption was observed at the pH range of 2-3. They noted that at very high pHs, there is a possibility of the formation of metal complexes and metal deposition (2). Therefore, in the present study, pHs 5 and 4 were considered as the optimal pH for removal of copper and lead by tea pulp, and at higher pHs, there is a possibility of removal due to deposition.

Adsorption of copper and lead was rapid at first but decreased over time. The adsorption equilibrium times for copper and lead were 45 and 30 minutes, respectively. The rate of metal adsorption decreased over time, and after equilibrium, the amount of metal adsorption remained constant. In adsorption processes, there are initially many empty adsorption sites on the adsorbent surfaces, so there is no competition between metal ions on the adsorbent sites. But over time, available places to adsorb other ions are limited. Due to the repulsive force between the ions adsorbed on the adsorbent surfaces and the ions present in the solution, it is difficult to adsorb more metal ions



**Figure 6.** Langmuir isotherm (a) and Freundlich isotherm (b) for adsorption of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  by tea waste.

**Table 3.** Parameters of kinetic models for adsorption of copper and lead by tea pulp

Heavy Metals	Pseudo-Second-Order			Intraparticle Diffusion			Elovich		
	R <sup>2</sup>	Q <sub>e</sub> (mg.g <sup>-1</sup> )	k <sub>2</sub> (g (min.mg) <sup>-1</sup> )	R <sup>2</sup>	C	KP (mg (min <sup>1/2</sup> .g) <sup>-1</sup> )	R <sup>2</sup>	b (g.mg <sup>-1</sup> )	a (mg (g.min) <sup>-1</sup> )
Cu <sup>2+</sup>	0.99	20.08	0.017	0.30	15.35	0.25	0.59	1.79	10.44
Pb <sup>2+</sup>	0.99	22.47	0.020	0.32	19.44	0.15	0.60	1.05	16.06

**Table 4.** Physicochemical properties of wastewater from copper and battery industries

Type of Industry	Parameters						
	pH	EC (ds/m)	Lead Concentration (ppm)	Copper Concentration (ppm)	BOD (mg/L)	COD (mg/L)	TDS (mg/L)
Battery industry	6.3	3.8	55.07	2.6	168	334	1098
Copper industry	4.3	4.2	2.1	5.21	67	179	277

**Table 5.** Comparative evaluation of removal efficiency of tea pulp with various adsorbents to removal of Pb (II) and Cu (II)

Entry	Adsorbents	Adsorption Capacity (mg/g)			Ref.
		Pb (II)	Cu (II)	Cd <sup>+2</sup>	
1	Grape Peels	69	60	-	(27)
2	Modified banana shell	-	-	16	(28)
3	Corn stalk graft	-	-	22.7	(29)
6	Orange peel	76.06	71.21	-	(30)
7	Tea pulp	48.54	37.17	-	This work

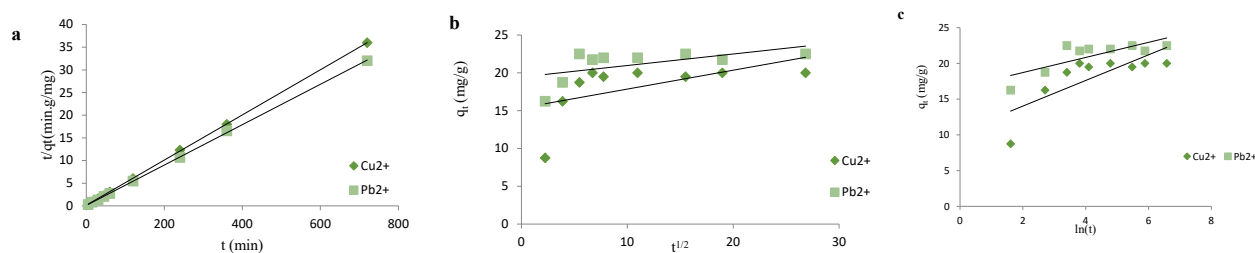
(35,36). Therefore, the adsorption rate decreased over time until it reached equilibrium.

Adsorption capacity of copper and lead (in single and competitive adsorption mode) increased with increasing heavy metal concentration, but its removal percentage decreased. The decrease in heavy metal removal percentage can be explained by the fact that adsorbents have limited adsorption surfaces and when adsorption surfaces are filled by heavy metal, adsorption is limited. Therefore, with increasing initial concentration, the removal percentage of both heavy metals decreases. The increase in adsorption capacity is due to the increase in concentration gradient and the driving force created by it because the concentration gradient and the resulting driving force increase with increasing initial concentration of heavy metal (37, 38).

In both single-element and competitive two-element adsorption, lead adsorption is greater than copper

adsorption. This result is consistent with the results of other researchers on the adsorption of heavy metals by organic matter. For example, Park et al. (2016) in South Korea studied the adsorption of various heavy metals on biochar prepared from sesame straw and their results showed that in both single-element and multi-element competitive adsorption, lead adsorption was greater than copper uptake (38). In China, Inyang et al examined the ability of two types of sewage sludge to adsorb lead, copper, nickel, and cadmium, and their results showed that lead uptake by both types of sewage sludge was higher than the uptake of other metals (39).

Uchimiya et al in the United States studied the stabilization and uptake of heavy metals (lead, copper, nickel, and cadmium) by soil in the presence of biochar organic matter, and the uptake of lead and copper was maximum, respectively (40). The results of the study of Inyang et al in China showed that the uptake of heavy metals from aqueous solutions by peanut biochar was in order of nickel < cadmium < copper < lead. The higher adsorption of lead compared to copper may be due to the higher electronegativity of lead. According to the electronegativity series, the sequence of adsorption of heavy metals by different adsorbents should be in the order of < chromium < cadmium < copper < lead, as the results of this study for copper and lead follow this series (39). The prediction of higher lead uptake compared to copper can be explained based on the Misono softness parameter presented by Sposito in the United States (41). Based on this parameter, the adsorption prediction is

**Figure 7.** Pseudo-second-order (a), intraparticle diffusion (b), and Elovich (c) models for adsorption of Cu<sup>2+</sup> and Pb<sup>2+</sup> by tea waste .

based on the first hydrolysis constant, which is higher for Pb. The Misono softness parameter is an indicator that is determined by the ionic radius and the ionization potential of the metal (41). In Malaysia, Ashraf et al investigated the removal of lead, copper, zinc, and nickel from banana peels. Lead removal efficiency was higher than copper, which is consistent with the results of this study (42). A study conducted by Ghasemi et al in Iran showed that the high removal efficiency of cadmium by tea wastes is an effective and cost-effective method for removing heavy metals from aqueous solutions without the need for any chemicals. The reason for this finding, as can be seen in the results of this study, is the fibrous and networked nature of the adsorbent tissue (43). A study conducted by Patil et al in India showed that tea waste is a bioadsorbent with a high adsorption capacity of pharmaceutical contaminants, which confirms the adsorption power of tea waste as a bioadsorbent (44).

### Conclusion

According to the results of this study, the use of Iranian tea pulp due to its high capacity to adsorb lead (more than 40 mg/g) and copper (more than 30 mg/g) can be effective for wastewater and water treatment. Also, the presence of heavy metals and other cations affects the adsorption capacity of metals by tea pulp and the competition of different cations reduces the efficiency of tea pulp for purification. Therefore, when using tea pulp on a real sample, the issue of competition between other metal cations should be carefully considered so that the applied amount of tea pulp is applied correctly and the refining operation is highly efficient and economical. As a result, the use of organic matter such as tea pulp is an effective and inexpensive technique for removing heavy metals from contaminated water.

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### Ethical issues

The authors certify that all data collected during the study are as stated in the manuscript, and no data from the study has been or will be published elsewhere separately (The Ethic approval Code: IR.KMU.REC.1400.377).

### Competing interests

The authors declare that they have no conflict of interests.

### Author's contributions

All authors were equally involved in the data collection, analysis, and interpretation. All authors critically reviewed, refined, and approved the manuscript.

### References

- Glatstein DA, Francisca FM. Influence of pH and ionic strength on Cd, Cu and Pb removal from water by adsorption in Na-bentonite. *Appl Clay Sci* 2015; 118:61-7. doi: 10.1016/j.clay.2015.09.003.
- Amarasinghe B, Williams R. Tea waste as a low cost adsorbent for the removal of Cu and Pb from wastewater. *Chem Engin J* 2007; 132(1-3):299-309. doi: 10.1016/j.cej.2007.01.016.
- Tunali S, Cabuk A, Akar T. Removal of lead and copper ions from aqueous solutions by bacterial strain isolated from soil. *Chem Engin J* 2006; 115(3):203-11. doi: 10.1016/j.cej.2005.09.023.
- Dai Y, Sun Q, Wang W, Lu L, Liu M, Li J, et al. Utilizations of agricultural waste as adsorbent for the removal of contaminants: A review. *Chemosphere* 2018; 211: 235-253. doi: 10.1016/j.chemosphere.2018.06.179.
- Jawad AH, Rashid RA, Mahmud RM, Ishak MAM, Kasim NN, Ismail K. Adsorption of methylene blue onto coconut (*Cocos nucifera*) leaf: optimization, isotherm and kinetic studies. *Desalination Water Treat* 2016; 57(19):8839-53. doi: 10.1080/19443994.2015.1026282.
- Rosales E, Mejjide J, Pazos M, Sanromán MA. Challenges and recent advances in biochar as low-cost biosorbent: From batch assays to continuous-flow systems. *Bioresource Technol* 2017; 246:176-192. doi: 10.1016/j.biortech.2017.06.084.
- Malakootian M, Pournamdari M, Asadipour A. et al. Degradation and removal of p-nitroaniline from aqueous solutions using a novel semi-fluid Fe/charcoal micro-electrolysis reactor. *Korean J Chem Eng* 2019; 36: 217-225. doi: 10.1007/s11814-018-0166-x.
- Malakootian M, Dadban Shahamat Y, Mahdizadeh H. Purification of diazinon pesticide by sequencing batch moving-bed biofilm reactor after ozonation/Mg-Al layered double hydroxides pre-treated effluent. *Sep Purif Technol* 2020; 242:116754. doi: 10.1016/j.seppur.2020.116754.
- Malakootian M, Nasiri A, Alibeigi A. et al. Synthesis and stabilization of ZnO nanoparticles on a glass plate to study the removal efficiency of acid red 18 by hybrid advanced oxidation process (ultraviolet/ZnO/ultrasonic). *Desalin Water Treat* 2019; 170: 325-336. doi: 10.5004/dwt.2019.24728.
- Malakootian M, Nasiri A, Mahdizadeh H. Preparation of CoFe<sub>2</sub>O<sub>4</sub>/activated carbon@chitosan as a new magnetic nanobiocomposite for adsorption of ciprofloxacin in aqueous solutions. *Water Sci Technol* 2018; 78(10):2158-2170. doi: 10.2166/wst.2018.494.
- Malakootian M, Nasiri A, Mahdizadeh H. Metronidazole adsorption on CoFe<sub>2</sub>O<sub>4</sub>/Activated Carbon@Chitosan as a new magnetic biocomposite: modelling, analysis, and optimization by response surface methodology. *Desalin Water Treat* 2019; 164: 215-227. doi: 10.5004/dwt.2019.24433.
- Mashhadi S, Javadian H, Ghasemi M, Saleh TA, Gupta VK. Microwave-induced H<sub>2</sub>SO<sub>4</sub> activation of activated carbon derived from rice agricultural wastes for sorption of methylene blue from aqueous solution. *Desalination Water Treat* 2016; 57(44):21091-104. doi: 10.1080/19443994.2015.1119737



13. Nasiri A, Malakootian M, Shiri MA, Yazdanpanah G, Nozari M. CoFe<sub>2</sub>O<sub>4</sub>@methylcellulose synthesized as a new magnetic nanocomposite to tetracycline adsorption: modeling, analysis, and optimization by response surface methodology. *J Polym Res* 2021; 28(5):192. doi:10.1007/s10965-021-02540-y.
14. Malakootian M, Mahdizadeh H, Khavari M, Nasiri A, Amiri Gharaghani M, Khatami M, et al. Efficiency of novel Fe/charcoal/ultrasonic micro-electrolysis strategy in the removal of Acid Red 18 from aqueous solutions. *J Environ Chem Eng* 2020;8(2):103553. doi: 10.1016/j.jece.2019.103553.
15. Kadirvelu K, Kavipriya M, Karthika C, Radhika M, Vennilamani N, Pattabhi S. Utilization of various agricultural wastes for activated carbon preparation and application for the removal of dyes and metal ions from aqueous solutions. *Bioresour Technol* 2003; 87(1):129-32. doi: 10.1016/s0960-8524(02)00201-8.
16. Salem NA, Yakoot SM. Non-steroidal Anti-inflammatory Drug, Ibuprofen Adsorption Using Rice Straw Based Biochar. *Int J Pharmacol* 2016; 12(7):729-736. doi: 10.3923/ijp.2016.729.736.
17. Gupta H, Gupta B. Adsorption of polycyclic aromatic hydrocarbons on banana peel activated carbon. *Desalin Water Treat* 2016; 57(20):9498-9509. doi: 10.1080/19443994.2015.1029007.
18. Tang R, Dai C, Li C, Liu W, Gao S, Wang C. Removal of methylene blue from aqueous solution using agricultural residue walnut shell: equilibrium, kinetic, and thermodynamic studies. *J Chemistry* 2017;1-10. doi: 10.1155/2017/8404965.
19. Gámiz B, Pignatello JJ, Cox L, Hermosín MC, Celis R. Environmental fate of the fungicide metalaxyl in soil amended with composted olive-mill waste and its biochar: An enantioselective study. *Sci Total Environ* 2016; 541:776-783. doi: 10.1016/j.scitotenv.2015.09.097.
20. Safa Y. Utilization of mustard and linseed oil cakes: novel bioadsorbents for removal of acid dyes. *Desalin Water Treat* 2016; 57(13):5914-5925. doi : 10.1080/19443994.2015.1007087.
21. Trivedi NS, Mandavgane SA, Kulkarni BD. Mustard plant ash: a source of micronutrient and an adsorbent for removal of 2,4-dichlorophenoxyacetic acid. *Environ Sci Pollut Res Int* 2016; 23(20):20087-20099. doi: 10.1007/s11356-016-6202-7.
22. Smitha T, Santhi T, Prasad AL, Manonmani S. Cucumis sativus used as adsorbent for the removal of dyes from aqueous solution. *Arabian J Chemistry* 2017; 10:S244-S251. doi: 10.1016/j.arabjc.2012.07.030.
23. Lee LY, Gan S, Tan MSY, Lim SS, Lee XJ, Lam YF. Effective removal of Acid Blue 113 dye using overripe Cucumis sativus peel as an eco-friendly bioadsorbent from agricultural residue. *J Cleaner Produc* 2016; 113:194-203. doi: 10.1016/j.jclepro.2015.11.016.
24. Mazaheri-Tehrani M, Dabbagh R, Nafar A. Biological removal of Lead from aqueous solutions using low-cost bio sorbents. *Feyz* 2013; 16(7):745-746. [Persian]
25. Mohammed RR. Removal of heavy metals from waste water using black teawaste. *Arabian J Sci Engin* 2012; 37(6):1505-1520. doi:10.1007/s13369-012-0264-8.
26. Weng CH, Lin Y-T, Hong DY, Sharma YC, Chen SC, Tripathi K. Effective removal of copper ions from aqueous solution using base treated black tea waste. *Ecologic Engin* 2014; 67:127-133. [Persian] doi: 10.1016/j.ecoleng.2014.03.053.
27. Shartooh S, Gabur H. The removal of lead, copper and zinc from industrial wastewater using grape fruit peels. *Rafidain Journal of Science* 2014; 25(2):22-31. doi.org/10.33899/rjs.2014.88565.
28. Mehrasbi M. Heavy metal removal from aqueous solution by adsorption on modified banana shell. *Iranian Journal of Health and Environment* 2008; 1(1):57-66.
29. Zheng L, Dang Z, Zhu C, Yi X, Zhang H, Liu C. Removal of cadmium (II) from aqueous solution by corn stalk graft copolymers. *Bioresour Technol* 2010; 101(15):5820-6. doi: 10.1016/j.biortech.2010.03.013.
30. Malakootian M, KHazaei A, Loloie M. Investigation of Fe<sub>3</sub>O<sub>4</sub> nanoparticles modified with orange peel efficiency in removal of lead and copper ions from aqueous environments. *Toloo-e-Behdasht* 2014; 13(2):1-11. [Persian]
31. Afroze S, Sen TK. A review on heavy metal ions and dye adsorption from water by agricultural solid waste adsorbents. *Water Air Soil Pollut* 2018; 229(7):1-50. doi:10.1007/s11270-018-3869-z.
32. Karmaker S, Uddin MN, Ichikawa H, Fukumori Y, Saha TK. Adsorption of reactive orange 13 onto jackfruit seed flakes in aqueous solution. *J Environ Chemical Engin* 2015; 3(1):583-592. doi: 10.1016/j.jece.2014.09.010.
33. Jain CK, Malik DS, Yadav AK. Applicability of plant based bioadsorbents in the removal of heavy metals: a review. *Environ Process* 2016; 3(2):495-523. doi:10.1007/s40710-016-0143-5.
34. Wu CH, Kuo CY, Guan SS. Adsorption kinetics of lead and zinc ions by coffee residues. *Pol J Environ Stud* 2015; 24(2):761-767. doi:10.15244/pjoes/31222.
35. Hossain M, Ngo HH, Guo W, Nguyen T. Removal of copper from water by adsorption onto banana peel as bioadsorbent. *Int J Geomate* 2012; 2(2):227-234. doi. org/10.21660/2012.4.3c.
36. Lodeiro P, Barriada JL, Herrero R, Sastre de Vicente ME. The marine macroalga *Cystoseira baccata* as biosorbent for cadmium (II) and lead (II) removal: kinetic and equilibrium studies. *Environ Pollut* 2006; 142(2):264-73. doi: 10.1016/j.envpol.2005.10.001.
37. Mazloomi F, Jalali M. Ammonium removal from aqueous solutions by natural Iranian zeolite in the presence of organic acids, cations and anions. *Journal of Environmental Chemical Engineering* 2016; 4(1):240-249. doi: 10.1016/j.jece.2015.11.001
38. Park JH, Ok YS, Kim SH, Cho JS, Heo JS, Delaune RD, et al. Competitive adsorption of heavy metals onto sesame straw biochar in aqueous solutions. *Chemosphere* 2016; 142:77-83. doi: 10.1016/j.chemosphere.2015.05.093.
39. Inyang M, Gao B, Yao Y, Xue Y, Zimmerman AR, Pullammanappallil P, Cao X. Removal of heavy metals from aqueous solution by biochars derived from anaerobically digested biomass. *Bioresour Technol* 2012; 110:50-6. doi: 10.1016/j.biortech.2012.01.072.
40. Uchimiya M, Chang S, Klasson KT. Screening biochar's for heavy metal retention in soil: role of oxygen functional

- groups. *J Hazard Mater* 2011; 190(1-3):432-41. doi: 10.1016/j.jhazmat.2011.03.063.
41. Sposito G. *The chemistry of soils*. Oxford: Oxford university press; 2008.
42. Ashraf MA, Wajid A, Mahmood K, Maah MJ, Yusoff I. Low cost biosorbent banana peel (*Musa sapientum*) for the removal of heavy metals. *Sci Res Essays* 2011; 6(19):4055-4064. doi: 10.5897/sre11.303.
43. Ghasemi S, Mafi Gholami R, Yazdanian M. Biosorption of heavy metal from cadmium rich aqueous solutions by tea waste as a low cost bio-adsorbent. *Jundishapur J Health Sci* 2017 ; 9(1):e37301. doi: 10.17795/jjhs-37301.
44. Patil CS, Gunjal DB, Naik VM, Harale NS, Jagadale SD, Kadam AN, et al. Waste tea residue as a low cost adsorbent for removal of hydralazine hydrochloride pharmaceutical pollutant from aqueous media: An environment remediation. *J Clean Prod* 2019; 206:407-418. doi: 10.1016/j.jclepro.2018.09.140.