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Biosorption of Fe (III) onto coffee and tea powder: Equilibrium and kinetic study

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ARTICLE INFORMATION

ABSTRACT

The coffee and tea powders were investigated to be as a novel low-cost non-conventional biosorbent for the removal of Fe (III) from aqueous solutions. Biosorption isotherms and kinetics were also assessed. The studied operating parameters were initial Fe (III) concentration, contact time, pH, and biosorbent dose. The adsorption capacity was significantly increased from 9.18 mg/g to 54.14 mg/g when the initial metal ion concentration increased from 20 to 120 ppm. However, the adsorbed amount of Fe was improved from 2.29 to 23.31 mg/g when the biosorbent dose decreased from 1.0 to 0.1 g. Biosorption isothermal data could be well simulated by Langmuir, Freundlich, and then Temkin models denoted by high correlation coefficient values (R2 > 0.95). However, the Dubinin-Radushkevich isotherms model gives the least fit to experimental data. Langmuir adsorption capacities of coffee and tea were 85.5 and 285 mg/g, respectively. The kinetic data fitted very well to the pseudo-second-order kinetic model. As indicated by the biosorption capacity, coffee and tea powder are considered to be an efficient, low cost, and environmentally friendly biosorbent for the removal of Fe (III) ions from aqueous solutions.

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Graphical Abstract

Introduction

Contamination of the surface and ground water resulted from human and industrial actions has been considered as a main problem all over the world. Consistently, there are a huge of chemicals release directly and indirectly into water resourcers without any treatment for removal of the harmful chemicals. Heavy metals are certainly well thought-out as the main hazardous and hurtful chemicals even if they are in trace levels, because they accumulate in the tissue of living organisms [1]. The aqueous waste streams from metal plating, textile industries, tanneries, and other industries are contaminated with heavy metals. Heavy metals are toxic, carcinogenic, and cause serious health problems even in very low levels [2, 3].

Iron is the most rich metal in the earth, and the essential biological nutrient for the most living organisms as it is the cofactor for considerable vital proteins and enzymes. Respiration process of various aerobic organisms are supported by iron mediated reactions. However, iron also can catalyze radical formation reactions if it is not shielded properly. These series reactions can damage tissues, cells, biomolecules, and the whole organism. Iron toxicity has constantly been a subject of concern especially to pediatricians. The risk of cancer is increased by excess iron uptake and it is a serious problem in developed and meat eating countries [4].

Various methods for removing the heavy metals from industrial waste water could be used. These methods include filtration [5], chemical precipitation [6], reverse osmosis [7], ion-exchange, coagulation [8], membrane filtration, and others [9–16]. These techniques can decrease heavy

metal concentrations, but the high material and operational costs lead to the limitations of using these methods. Among several available metal extraction techniques, adsorption is considered to be the most promising choice for the removal of heavy metals from aqueous solutions, activated carbons being the most popular adsorbent due to their efficiency and versatility. Activated carbon as an adsorbent has been vastly examined for the adsorption of the heavy metals, but its high-cost restrict its commercial usage. Moreover, some difficulties have been described for activated carbon in terms of engineering complications such as considerable diffusion resistance and regeneration efficiency [17]. To overcome these shortcomings, the use of low cost and abundant biomass adsorbent has attracted much attention lately. The widespread use of biosorbents for wastewater treatment is strongly recommended due to their low operational cost, local availability, and engineering applicability [18].

In our previous work, we used olive leaves and orange peels powders as biosorbents for removing Fe (III) from aqueous solutions [19, 20]. In the present study, factors affecting the biosorption efficiency of Fe (III) by coffee and tea powders have been studied. Equilibrium and kinetic studies using various models have been also investigated.

Experimental

Materials and methods

All the used chemicals were of analytical reagent (AR) grade. 1000 ppm Fe (III) stock solution was prepared by dissolving an appropriate amount of $Fe(NO_3)_3$ salt in deionized water. The stock solution was diluted to the required concentrations using deionized water. The solution pH was adjusted using 0.10 M HCl or 0.10 M NaOH.

Determination of Fe (III)

The concentration of Fe^{+3} ions in the solutions before and after equilibrium was determined by Molecular Absorption Spectrophotometer 6305 from JENWAY. The pH of the solution was measured with pH Meter 3505 from JENWAY. The determination of iron (III) as thiocyanate complex was carried out according to the published work [21]. The range of calibration curve concentrations of metal ions prepared from stock solution varies between 1–10 ppm.

Preparation of adsorbents

The coffee and tea powders were collected from a coffee shop, washed with double distilled water and then dried in an oven at 70 °C for 24 h. The dried materials were sieved through 500 μm size fraction using an american society for testing and materials (ASTM) standard sieve.

Adsorption experiments

The adsorption experiments were carried out in a series of 150 mL erlenmeyer flasks containing 50 mL of metal ions solution, 0.100 g adsorbent powder and if necessary, an appropriate volume of HCl or NaOH solutions was used to adjust the pH of the solution. The solutions were shaken (175 rpm) at 25 °C. Then solutions were filtered by the whatman filter paper. The removal percentage (% R) was calculated using the following equation.

$$\% \, R = \frac{C_o - C_e}{C_o} \, X \, 100 \tag{1}$$

where: C_o and C_e are the initial and final concentrations in ppm, respectively. The amount of adsorbed metal (mg metal per gram adsorbent) was calculated based on the difference between the initial (C_o, ppm) and final concentration (C_e, ppm) in every flask, as follows.

$$Q_e = \frac{C_o - C_e}{M} \, X \, V \tag{2}$$

where Q_e is the metal uptake capacity (mg/g), V the volume of the metal solution in the flask (L) and M is the dry mass of biosorbent (g).

Parameters affecting adsorption experiments

The following experiments were carried out to study the influence of pH, biosorbent dose, contact time, and metal ion concentration on adsorption of iron onto coffee and tea powders. *I*) The pH dependent study was carried out in series of 50 mL aqueous solutions of 25 ppm Fe (III) and containing 0.1 g powder. The investigated pH values for these solutions were varied between 1.5 to 7. The contact time was set at 30 min. *II*) The effect of contact time on Fe (III) adsorption was examined for series of 50 mL solutions with 25 ppm concentration and containing 0.1 g powder. The pH for all solutions was set to the optimum from (1). The contct time was varied for each solution between 10–60 min. *III*) The effect of biosorbent doses on metal uptake was investigated using series solutions with adsorbent masses of 0.1, 0.2, 0.4, 0.6, 0.8, and 1 g per 50 mL of 50 ppm Fe (III) solution. The optimum pH and contact time were chosen. *IV*) Finally, various concentrations of Fe (III) were investigated to study the effect of metal ion concentration which were: 20, 40, 60, 80, 100, 120 ppm per 50 mL solution containg 0.1 g biosorbent. The optimum pH and contact time were chosen.

Results and discussion

Effect of pH on biosorption process

The functional groups on the adsorption surface and the metal ion state are controlled by solution pH. The percent removal of Fe (III) from aqueous solution onto coffee and tea powders were affected by the pH (Figure 1).

The percent removal was increased from 55 to 95% with the increase the pH from 1.75 to 7. The optimum pH value for the Fe (III) adsorption onto coffee and tea powders was selected to be between 5.5 and 6 for further study. Low percent removal were observed at low pH values since the H_3O^+ ions compete with the Fe^{+3} for binding and also surrounded (H_3O^+) will prevent the iron ions from approaching the binding sites. However, at higher pH, (Above pH 7), the Fe (III) started precipitating, so the removal was not achieved only by adsorption.

Effect of time on biosorption process

The percent removal of Fe (III) as a function of time is shown in Figure 2. From the Figure below, it is indicated that the kinetic of the adsorption process is fast and about 75 and 90% of Fe (III) were adsorbed after 30 min for coffee and tea, respectively. A further increase in the adsorption time (Up to 60 min) does not significantly improve Fe (III) uptake. Therefore, the time of equilibration was fixed at 30 min in the all further experiments.

Effect of metal ion concentration on biosorption process

The initial Fe (III) concentration was changed from 20–120 ppm in order to study the adsorption isotherm of the biosorbent process. The dependent of biosorption capacity of metal ion is shown in Figure 3. From the Figure, the adsorption capacity increases as the initial Fe (III) concentration increases. This is because of the increase of the driving force (Gradient of Fe (III) concentration). Therefore, Fe (III) ions are favorably adsorbed at higher concentrations, even though, it is also possible even at lower concentrations.

Effect of biosorbent mass on biosorption process

The potential of adsorbent to remove Fe (III) from its solution is determined by the initial concentration [22]. The removal efficiency (%) and adsorption capacity (mg/g) as a function of biosorbent dose are shown in the Figures 4 and 5, respectively. They are revealed that on increasing adsorbent dose from 0.1 to 1 g, the percent removal increases and adsorption capacity decreases. This trends are also observed in our earlier work [19, 20]. With increasing adsorbent dose, more surface area and active sites are available for adsorption [23] and therefore the percent removal increases. However, adsorption capacity decreases as biosorbent dose increases. This could be explained by: *I*) number of adsorption sites remain unbounded during the biosorption

process, *II*) the external surface area is reduced by the agglomeration of biomass particles at higher doses, *III*) desorption of Fe (III) could occur at high adsorbent doses because of particles interaction [2].

Biosorption isotherms

Distribution of the metal ions between biosorbent (Solid phase) and solution (liquid phase) can be described by isotherms model when the system reached the equilibrium. Various isotherm models have been used to describe this interaction. The adsorption isotherms models used in our study are including Langmuir [24], Freundlich [25], Temkin [26], and Dubinin-Radushkevich (D-R) models [27].
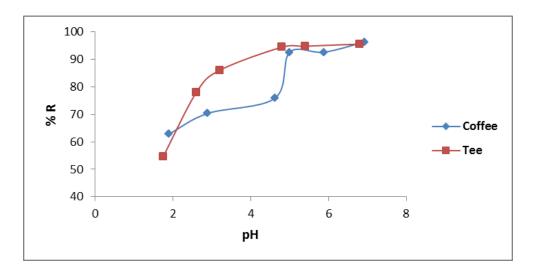

Figure 1. Effect of pH on biosorption of Fe (III) onto coffee and tea powders
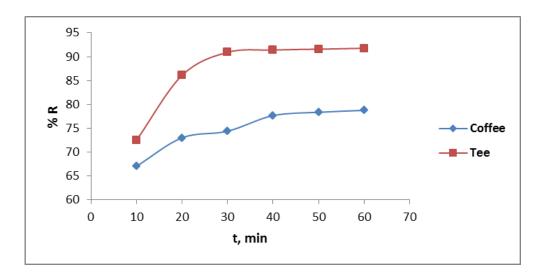

Figure 2. Effect of time on biosorption of Fe (III) onto coffee and tea powders
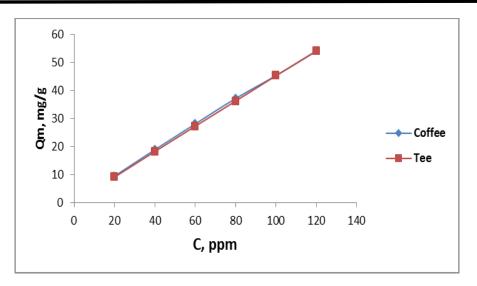
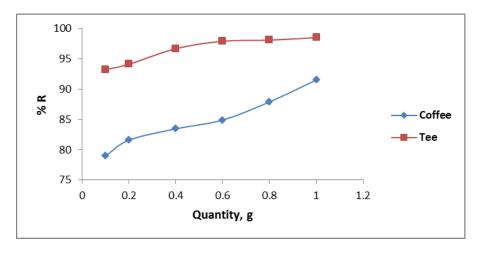**Figure 3.** Effect of metal ion concentration on biosorption capacity of Fe (III) onto coffee and tea powders

Figure 4. Effect of biosorbent dose on biosorption efficiency of Fe (III) onto coffee and tea powders
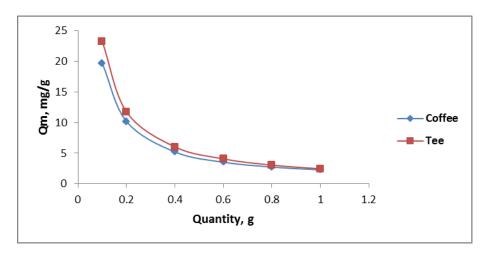

Figure 5. Effect of biosorbent dose on biosorption capacity of Fe (III) onto coffee and tea powders

Langmuir isotherm

Langmuir isotherm model assumes that the adsorption occurs at monolayer surface with a finite number of identical sites.The linearized form of Langmuir equation is described in equation (3).

$$\frac{1}{Q_e} = \frac{1}{Q_m} + \frac{1}{b\,Q_m\,C_e} \tag{3}$$

where b is the Langmuir constant related to the energy of adsorption, C_e is the equilibrium concentration of Fe (III) in ppm, Q_e is the milligrams of metal adsorbed per gram of adsorbent (mg/g), and Q_m is maximum adsorption capacity (mg/g). Values of Langmuir parameters Q_m and b were evaluated from the slope and intercept of linear plot of $1/Q_e$ vs. $1/C_e$ as shown in Figure 6. The evaluated parameters are given in Table 1. The values of R^2 (> 0.999) indicated that adsorption of Fe (III) onto coffee and tea powders best fitted to Langmuir model.

The essential features of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor R_L which is used to predict the adsorption system is favorable or unfavorable and is given by equation (4).

$$R_L = \frac{1}{1 + b\,C_0} \tag{4}$$

where b is the Langmuir equilibrium constant and C_0 is the initial metal ion concentration in ppm. The value of R_L indicated the type of Langmuir isotherm to be irreversible (R_L=0), favorable (0 < R_L < 1), linear (R_L=1), or unfavorable (R_L > 1). The value of R_L was found less than 1 and greater than zero in the adsorbents. This confirms that the Langmuir isotherm model is favorable for adsorption of Fe (III) onto coffee and tea powders.

Freundlich isotherm

Freundlich isotherm model is used to describe adsorption on a surface having heterogeneous energy distribution. The linear form of isotherm is given by equation (5).

$$Log\,Q_e = Log\,K_f + \frac{1}{n}\,Log C_e \tag{5}$$

where K_f is Freundlich constant related to the bonding energy. $1/n$ is the heterogeneity factor and n is a measure of the deviation from linearity of adsorption. Freundlich parameters can be determined from the plot of log Q_e vs log C_e, as shown in Figure 7. The degree of non-linearity between solution concentration and adsorption can be predicted from n value. If n=1, then

adsorption is linear; if n < 1, adsorption is a chemical process; finally if n > 1, then adsorption is a physical process. The n values were found to be 1.50 and 1.09 for coffee and Tea, respectively, as given in Table 1, which indicate the physical biosorption of Fe (III) onto coffee and tea powders. The values of R^2 indicated good fitted of the experimental data to the Freundlich model.

Temkin isotherm

The Temkin isotherm model assumes that the adsorption energy decreases linearly with the surface coverage due to the adsorbate-adsorbent interaction. The linear form of the Temkin isotherm model is given by the equation (6).

$$Q_e = B \ Log \ A + B \ Log \ C_e \tag{6}$$

where Q_e is the metal adsorbed in milligrams per gram of adsorbent, C_e concentration of the adsorbate at equilibrium in ppm, A is the equilibrium binding constant, and B corresponds to the heat of sorption. $B = RT/b_T$ where R is the ideal gas constant (8.314 J.mol^{-1}.K^{-1}) and T is the temperature in Kelvin, b_T is the Temkin isotherm constant. Temkin parameters can be determined from the plot of Q_e vs log C_e, as shown in Figure 8. The values of A and B just determined are given in Table 1. The values of R^2 indicated that the experimental data are not good fitted, as Langmuir and Freundlich models, to the Temkin model.

Dubinin-radushkevich (D-R) isotherm

Dubinin-radushkevich (D-R) model was also used to test the experimental data. The equation 7 is the linear form of the D-R isotherm model.

$$Log \ Q_e = Log \ Q_d - \beta \ \varepsilon^2 \tag{7}$$

where ε is correlated to C_e (ppm) by the Equation (8):

$$\varepsilon = RT \ Log \left(1 + \frac{1}{C_e}\right) \tag{8}$$

where T is the absolute temperature (K) and R is the gas constant (8.314 J.mol^{-1}.K^{-1}). The D-R isotherm parameters β and Q_d can be obtained from the slope and intercept of the plot of ln Q_e vs ε^2 as shown in Figure 9. The vales are given in Table 1. The values of correlation coefficient R^2 were lower than that of other three isotherm values (0.94 and 0.95). The D-R model gives the least fit to experimental data than the other isotherms models.
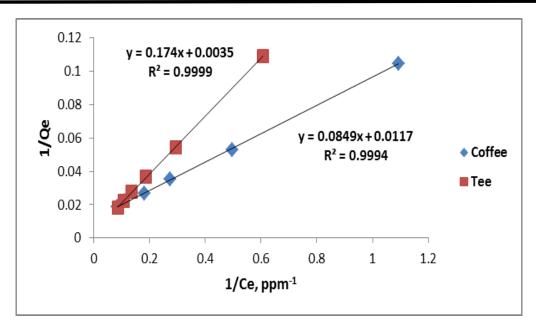
Biosorption Kinetics

Figure 6. Langmuir Isotherm for biosorption of Fe (III) onto coffee and tea powders

Table 1. Adsorption isotherm constants for adsorption of Fe (III) onto coffee and tea powders

Biosorbent	Coffee powder	Tea powder
	Langmuir parameters	
Q_m (mg/g)	85.47	285.71
b	0.14	0.02
R^2	0.9994	0.9999
R_L	0.13	0.5
	Freundlich parameters	
K_f	11.12	5.88
n	1.50	1.09
R^2	0.9849	0.9997
	Temkin Model	
A	1.64	1.33
B	39.57	52.63
b_T	62.61	47.08
R^2	0.9794	0.9437
	D-R Model	
Q_d	40.06	45.96
β	3×10^{-6}	9×10^{-6}
R^2	0.9398	0.9536

Two kinetic models, pseudo first-ordered and pseudo second-order have been fitted to the experimental data to examine the adsorption kinetics of Fe (III) uptake by coffee and tea powders.

Pseudo first-order kinetics

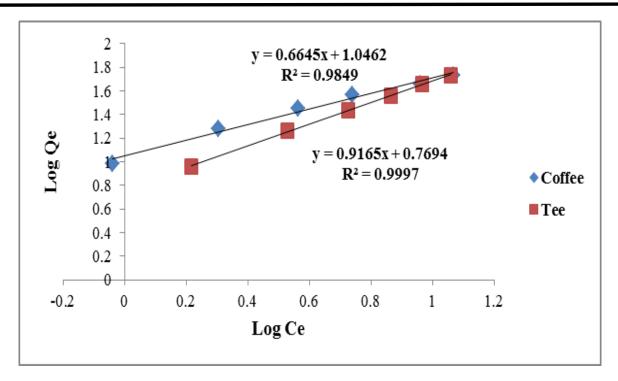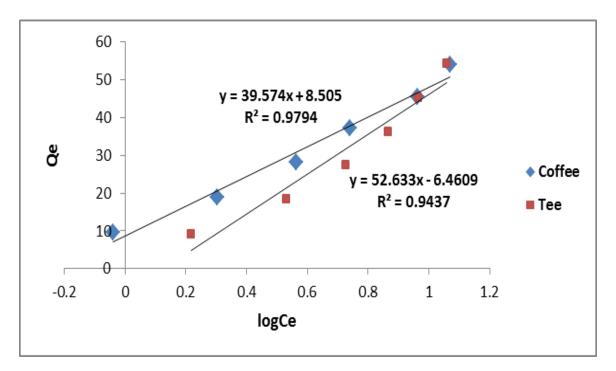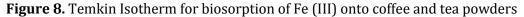Lagergren [28] equation for the pseudo-first order kinetics is expressed as follows

Figure 7. Freundlich Isotherm for biosorption of Fe (III) onto coffee and tea powders

Figure 8. Temkin Isotherm for biosorption of Fe (III) onto coffee and tea powders

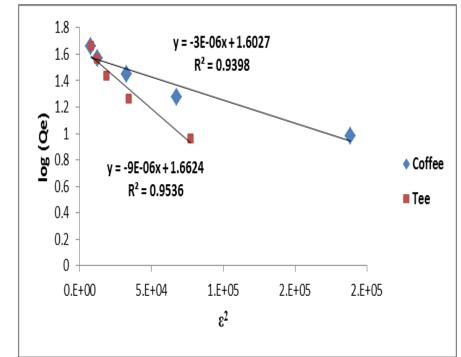$$Log \ (Q_e - Q_t) = \ Log \ Q_e - k_1 \ t \tag{9}$$

where Q_e (mg/g) is the metal uptake, Q_t (mg/g) is the metal uptake at time t, and k_1 (min^{-1}) is the rate constant of the pseudo-first-order adsorption. The rate constant can be determined from the linear plot of Log ($Q_e - Q_t$) against t (Figure 10). The Lagergren's pseudo-first-order rate constant (k_1), Q_e determined from the slope and intercept and correlation coefficients are given in Table 2. It was observed that the pseudo-first-order model did not fit well, showing that the adsorption of the Fe (III) did not follow the pseudo-first-order kinetics.
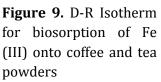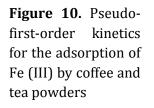
Pseudo second-order kinetics

The adsorption kinetics of Fe (III) onto coffee and tea powders can also be analyzed by the pseudo second- order equation [29].

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t \qquad (10)$$

where Q_e (mg/g) is the metal uptake at equilibrium, Q_t (mg/g) is the metal uptake at time t, and k_2 is the pseudo-second-order rate constant. The Q_e and k_2 values can be calculated from the slope and intercept of plot t/Q_t vs t (Figure 11). The values just determined are given in Table 2. The correlation coefficients were found to be 0.9991 and 0.9997. Therefore, the pseudo-second-order kinetic model is provided a better correlation for the adsorption of Fe (III) onto coffee and tea powders compared to the pseudo-first-order model.
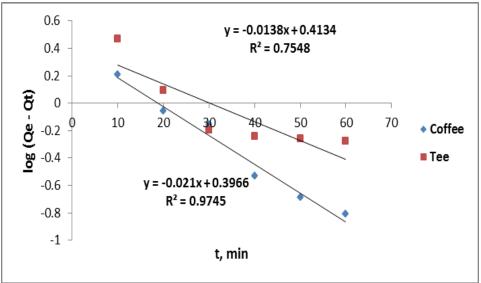
Figure 9. D-R Isotherm for biosorption of Fe (III) onto coffee and tea powders

Figure 10. Pseudo-first-order kinetics for the adsorption of Fe (III) by coffee and tea powders

Table 2. Pseudo-first-order and pseudo-second-order rate constants for adsorption of Fe (III) onto coffee and tea powders

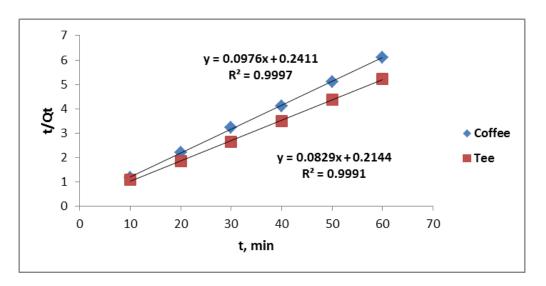| Biosorbent	Coffee powder	Tea powder
	Pseudo-first-order	
Q_e (mg/g)	2.49	2.59
k_1	0.021	0.014
R^2	0.9745	0.7548
	Pseudo-second-order	
Q_e	10.25	12.06
k_2	0.04	0.03
R^2	0.9997	0.9991

Figure 11. Pseudo-second-order kinetics for the adsorption of Fe (III) by coffee and tea powders

Conclusion

The potential of coffee and tea powders as high efficient, economical and green adsorbent for removing the Fe (III) ions from the aqueous solutions was examined in batch experiments as a function of contact time, initial pH, initial metal ion concentration, and biosorbent dose. The adsorption was significantly increased (> 400%) with the increase of initial metal ion concentration (From 20–120 ppm). However, the metal adsorption was also increased (> 900%) with the decrease of sorbate initial concentration (20.0–2.0 g/l). Equilibrium (Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich isotherms), and kinetics of the considered biosorption processes were investigated in details. Equilibrium was best fitted to the Langmuir isotherm ($R^2 >$ 0.999), while the kinetics of the process was best described by the pseudo-second-order model (also $R^2 >$ 0.999), suggesting monolayer coverage and a chemisorption process. The maximum metal capacities determined by using the Langmuir isotherm were 85.5 and 285 mg/g for coffee and tea powders, respectively. The results of our investigation indicate that the coffee and tea powders has a potential for use in removing Fe (III) from aqueous solutions.

Disclosure statement

No potential conflict of interest was reported by the authors.

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