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Biosorption of Pb(II) from aqueous solution by spent black tea leaves and separation by flotation

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ABSTRACT

The aim of this study was to investigate the ability of spent black tea leaves (SBTL) to remove lead from aqueous solution using biosorptive-flotation process. The biosorption process revealed that the SBTL was an effective biosorbent of lead and the maximum biosorption capacity was 19.7 mg/g after 180 min of contact time and at pH 5. Isotherm studies conducted at different initial metal concentration revealed the applicability of Freundlich isotherm model. Kinetic study explained the pseudo-first-order model as the best fit, suggesting that the biosorption process is presumably a physical sorption. Fourier transform infrared spectrometry indicated that the carboxyl, amino, and sulfonic groups on the biosorbent surface were the major groups responsible for the binding of lead ions. The flotation process, in which sodium dodecyl sulfate was used as a surfactant, increased the biosorption removal efficiency from 91 to 99%.

Keywords: Biosorption; Flotation; Lead; Tea leaves; Isotherm; Kinetics

1. Introduction

Heavy metal pollution has become a major issue in many countries because their existence in drinking water and wastewater often exceeds the permissible standards [1]. Heavy metals such as lead, copper, and cadmium are a sanitary and ecological threat. They are highly toxic and recalcitrant even at very low concentrations, and they can pollute drinking water resources [2,3]. Therefore, their removal from water and wastewater is important to protect public health. Heavy metals are often derived from heavy industry such as electroplating and battery factories, metal finishing, and chemical manufacturing. Biosorption is defined as the property of certain biomolecules to bind and concentrate selected ions or other molecules from aqueous solution [4]. The major advantage of biosorption technology is its effectiveness in reducing the concentration of heavy metal ions to very low levels in an environment-friendly manner [5]. Biosorbents fall under the following categories: bacteria, fungi, algae, yeast, and industrial and agricultural wastes [6–8]. After water, tea is the most widely consumed beverage in the world, as attested by the over 3,000,000 tons of tea leaves produced annually [9]. Although available in different varieties, such as green and black tea, all tea beverages are obtained from the same basic tea leaves (*Camellia sinensis* L.) [10]. Once the tea beverage has been brewed, the spent leaves become a waste that must be disposed as a municipal solid waste. As shown previously, the biosorption process has been proved to be an effective technique; however, it may

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suffer from some economic limitations owing to difficulties encountered in separating the sorbent from the aqueous solution [11]. Therefore, attempts have been made to develop separation techniques. One of the possible techniques for this scope is flotation. Separation by flotation has been widely used in industries for removing toxic metals as well as turbidity from aqueous solution. Turbidity represents an important aspect of water quality and is viewed as the cloudiness of liquid, caused by suspend and colloidal matter such as clay, silt, finely divided organic and inorganic matter, plankton, and other microorganisms [12]. Usually, turbidity is measured in nephelometric turbidity units (NTU) or Jackson turbidity units, depending on the method used for measurement. The main advantages of flotation process are simplicity, rapidity, good separation yield (>95%), large possibility of applications for species having different nature and structure, and flexibility and friability of equipment and processing for recovery purpose [13,14]. Owing to the aforementioned reasons, a combination of sorption and flotation into a unified operation, termed as sportive-flotation, could be considered as a vital process.

In this study, we focused on the use of spent black tea leaves (SBTL) as a biosorbent in batch system for the removal of lead ions (Pb(II)) from aqueous solutions. The biosorption process was followed by an air flotation process for separating the biosorbent and increasing the removal efficiency. SBTL was chosen as a biosorbent because this material is environmental-friendly, has low cost, and is widely available (obtained after cooking). Approximately, 4 kg of SBTL is generated daily from one of the coffee shops in Baghdad University, which is often collected with other garbage and dumped in a municipal solid waste landfill. The unit cost of collecting 1 kg of SBTL from one of the Baghdad University coffee shop is about US$ 0.2. The Pb(II) sorption was investigated considering the effects of pH, temperature, contact time, and initial metal concentration. The isotherms and kinetics of SBTL biosorption were studied to understand the sorption mechanism of Pb(II). Fourier transform infrared spectroscopy (FTIR) was applied to determine the surface functional groups responsible for the sorption process. Furthermore, the effect of air flow rate and collector concentration on the performance of the floatation process was also determined.

2. Materials and methods

2.1. Biosorbent and chemicals

In this study, SBTL was used as the biosorbent material. This material was collected from various restaurants after cooking. The foreign matter was removed from the SBTL and washed several times with tap water and distilled water to remove impurities. The washed SBTL was sun dried and then dried in oven at 50°C for 48 h. The dried material was shredded, ground into powder, sieved, and stored in an opaque air-tight polyethylene container at room temperature until use in the biosorption experiments. Mesh sizes of 0.4–0.6 mm particle diameter were used for the biosorption experiments. The SBTL biomass particle size distribution was determined using a set of standard sieves. As the biomass of SBTL could increase in water, the SBTL was initially soaked in distilled water and then wet sieved. A sample of powdered SBTL was analyzed for physical properties such as particle density, surface area, particle porosity, and bed void fraction. The surface area of SBTL was determined from N_2 adsorption isotherm analysis using a Micrometrics Nano Porosity System.

All the chemicals used in this study were of analytical grade, and deionized water was used for solution preparation. The stock solution (1,000 mg/l) of Pb (II) was prepared by dissolving appropriate weight of lead chloride in distilled water and stored in glass container at room temperature. The desired concentrations were prepared by diluting the stock solution in accurate proportions to different initial concentrations. The concentration of the metal was subsequently determined using flame atomic absorption spectrophotometer (AAS; SHIMADZU, Model: 7200, Japan). The initial pH of the working solutions was adjusted by addition of 1 mol/l NaOH or HCl using a pH meter (WTW, inoLab 720, Germany). Sodium dodecyl sulfate (SDS) was used as the anionic collector in the flotation experiments. All the glassware used for dilution, storage, and experimentation were cleaned with detergent, thoroughly rinsed with tap water, soaked overnight in a 20% HNO_3 solution, and finally rinsed with distilled water before use. Table 1 lists the properties of the biosorbent (SBTL), Pb(II) salt, and anionic collector (SDS) used in this study.

2.2. Effect studies

The effects of pH, temperature, contact time, and initial heavy metal concentration on the biosorption efficiency were studied as follows. To determine the effects of pH, six conical flasks, each containing 1 g of SBTL and 100 ml of 50 mg/l Pb(II) solution, were used. The pH of these solutions was adjusted to 2, 3, 4, 5, 6, and 7, respectively. A pH above 7 was excluded because Pb(II) may precipitate as hydroxide at this pH. The suspension was shaken at 200 rpm for 3 h using a shaker (Edmund Buhler, 7400 Tubingen Shaker-SM 25, Germany), and the residual amount of

Table 1
Properties of the SBLT, Pb(II) salt, and SDS used in this study

SBTL		Pb(II) salt		SDS	
Particle size (mm)	0.42	Salt	$PbCl_2$	Chemical structure	$C_{12}H_{25}OSO_3Na$
Surface area (m^2/g)	9.3	Appearance	White	Molecular weight (g/mol)	288
Bulk density (g/l)	0.52	Solubility (g/100 ml)	52	Appearance	White powder
Porosity (%)	60.5	Density (g/l)	4.53	Purity	99%
Moisture (%)	2.17	Company	Fluka	Company	Fisher Scientific

Pb(II) was determined using AAS after filtration. The temperature effect was determined using six conical flasks containing 100 ml of 50 mg/l Pb(II) solution at 15, 25, 35, 45, and 55°C, respectively, under constant shaking at 200 rpm for 3 h. To study the variation in the heavy metal removal efficiency at different initial Pb(II) concentrations, Pb(II) solutions with concentrations of 10, 50, 75, and 100 mg/l were employed with 1 g of SBTL. The pH of the solutions was fixed at 4, and the solutions were subjected to constant shaking at 200 rpm for 3 h. To detect the effect of contact time variation on the heavy metal removal efficiency, a beaker filled with 1,000 ml of 50 mg/l Pb(II) solution was subjected to constant shaking at 100, 150, 200, and 300 rpm, respectively, at an optimum pH determined in the pH study, then 10 g of SBTL was added to the solution. Subsequently, the samples were collected from 1 to 240 min to determine the remaining concentration of Pb(II).

2.3. Isotherm experiments

The biosorption isotherm of Pb(II) onto SBTL was investigated by performing batch mode sorption experiments. The experiments were conducted in 250 ml sealed conical flasks containing 100 ml of aqueous solution of heavy metal (1–50 mg/l) and 1 g of SBTL. The flasks were continuously shaken at room temperature (20 ± 3°C). The experiments were performed at the optimum pH and temperature values determined previously from the effect studies. Nine flasks were put in a shaker under a constant shaking speed (200 rpm) for 3 h. After biosorption, the sorbent was separated from the aqueous solution using a filter paper (WHATMAN, No. 42; diameter, 7 cm). The residual concentrations of Pb(II) were measured by AAS. Each sample was measured thrice, and the results were given as the average value. The biosorption capacity at equilibrium conditions (q_e) was calculated using the following equation:

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

where q_e is the equilibrium biosorption capacity (mg/g); C_0 and C_e are the initial and equilibrium adsorbate concentrations in water (mg/l), respectively; V is the volume of used solution (l); and m is the mass of used adsorbent (g).

The removal percentage of Pb(II) (%) was calculated using the following equation:

$$\%\ \text{Removal} = \left(\frac{C_0 - C_e}{C_0}\right) \times 100 \tag{2}$$

2.4. Kinetic study

The biosorption kinetic experiments were conducted in a beaker containing 10 g of SBTL and 1,000 ml of adsorbate solution under constant shaking at 200 rpm. The concentration of Pb(II) solution was 50 mg/l. Samples were collected at different time intervals to determine the Pb(II) content. The biosorption capacity for each time interval was calculated using Eq. (1).

2.5. Flotation experiments

Another series of experiments were conducted using flotation system to study the increase in the metal removal efficiency. In addition, the flotation process efficiency was also evaluated by measuring the residual content of supernatant turbidity. Fig. 1 shows the schematic diagram of the flotation experiment setup. The experiments were performed using a glass column of 6 cm in diameter and 120 cm in length. A 1 mm-thick stainless steel distributor with holes of 0.05 mm diameter was installed at the bottom of the

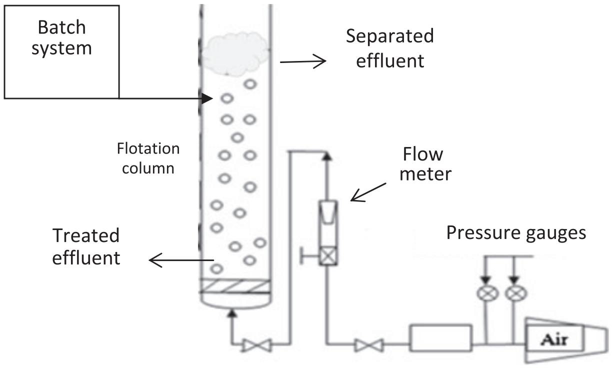

Fig. 1. Schematic diagram of the flotation experiment setup.

column for smooth distribution of air flow. The holes of the distributor were arranged in equilateral triangles. A feed air was supplied by the compressor (compressed at 1 bar up to 7 bars) through a pre-calibrated flowmeter. The air entering the column was dispersed as bubbles into the liquid. The steps of the biosorption–flotation experiment can be briefly described as follows: The metal was submitted to batch biosorption process until it reached the initial equilibrium time (>90% removal) using a beaker containing 1,000 ml of 50 mg/l Pb(II) solution and 10 g of SBTL (60 min of contact time and pH of 5 at room temperature and 300 rpm shaking speed). Then, the mixture of the metal solution with SBTL was poured gently at the top of the column (containing water and 50 g of SDS surfactant) and the flotation process was initiated. The column was previously pressurized to prevent seepage of the liquid through the holes. The flotation process was continued for 15 min, and samples were collected from the suspension every 5 min and analyzed for Pb(II) content and turbidity. After each experiment, the column was cleaned using HNO_3 and then rinsed thrice with distilled water. It should be noted that the optimum conditions determined from batch study were employed in the flotation experiments.

2.6. Isotherm and kinetic models

The experimental isotherm data were fitted with the two well-known sorption isotherm models, namely, Langmuir and Freundlich models. These two models are presented in Table 2. The Langmuir model is the simplest theoretical model for monolayer sorption onto a surface and assumes that all of the sorption sites have equal adsorbate affinity [15]. The Freundlich isotherm model is used for homogenous systems in which the heat of sorption decreases in magnitude with an increasing extent of sorption [16]. This model describes the ratio of the amount of solute that is adsorbed onto a given mass of adsorbent to the concentration of solute in the solution.

Kinetic models can be helpful for understanding the mechanism of sorption and evaluating the performance of an adsorbent. In this study, the sorption kinetics was modeled using the pseudo-first-order, pseudo-second-order, and intraparticle diffusion kinetic models. The equations of the kinetic models are presented in Table 2.

2.7. FTIR analysis

The infrared spectra of the powdered SBTL and Pb (II)-loaded SBTL samples were obtained using Fourier transform infrared spectroscope (Model: SHIMADZU 8500S). Normally, the spectra are measured within the range of 4,000–500 cm^{-1} [17].

3. Results and discussion

3.1. FTIR analysis

The FTIR spectra revealed the specific surface functional groups on the biosorbent based on the characteristic absorbed energy for each bonds in certain groups [23]. Fig. 2 shows the results of the observed IR absorption frequencies in different regions of SBTL before and after biosorption of Pb(II). The results showed that there were different functional groups on the surface of the SBTL. The broad peak detected in the spectra at 3,441 cm^{-1} can be assigned to the hydroxyl and amine groups (–OH and –NH) of alcohols, phenols, and carboxylic acids [24,25]. The peaks at 3,062, 2,920, and 2,850 cm^{-1} can be assigned to the alkyl chains (–C–H). The peaks in the region from 1720.5 to 1,431 cm^{-1} can be attributed to the presence of carboxylate, amide, sulfonate, and ketone groups (–C=O) [26]. The –C–O, C–C, and –C–OH stretching vibrations can be attributed to peaks in the region of 1,359–1,041 cm^{-1}. Some peaks in the fingerprint regions (900–750 cm^{-1}) could be attributed to the aromatic –C–H groups [27]. It can be observed from Fig. 2 that after the biosorption of Pb(II), some peaks were shifted or disappeared and new peaks were detected, suggesting that a binding process occurred on the surface of the biosorbent. Furthermore, non-symmetric shifting could also be noted mainly at 2,900–1,750 cm^{-1} and 900–500 cm^{-1}, with some peaks failing to exhibit any shifts mainly at 1,700–1,010 cm^{-1}. Thus, it can be concluded that the biosorption capacity of Pb(II) onto SBTL is influenced by the type and

Table 2
Equations for the sorption isotherm and kinetic models

Model	Equation	Linear expression	Reference
Langmuir	$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$	$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}$	[18]
	where q_e is the sorption uptake (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/ml), q_m isthe maximum amount of the adsorbate per unit weight of the adsorbent (mg/g), and K_L is the Langmuir constant and related to the free energy of sorption (L/mg)		
Freundlich	$q_e = K_F C_e^{1/n}$	$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$	[19]
	where q_e is the sorption uptake (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/L), n is the Freundlich constant related to sorption intensity (g/L), and K_F is the Freundlich constant related to the relative sorption capacity (mg/g)		
Pseudo-first-order	$q_t = q_e (1 - e^{-k_1 t})$	$\ln(q_e - q_t) = \ln q_e - k_1 t$	[20]
	where q_t is the metal uptake capacity (mg/g) at any time t, q_e is the metal uptake capacity (mg/g) at equilibrium, and $k_1$is the observed rate constant of pseudo-first-order kinetic model (1/min)		
Pseudo-second-order	$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}$	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$	[21]
	where q_t is the metal uptake capacity (mg/g) at any time t, q_e is the metal uptake capacity (mg/g) at equilibrium, and $k_1$is the observed rate constant of pseudo-second-order kinetic model (g/mg min)		
Intraparticle diffusion	$q_t = K_t t^{1/2} + C$		[22]
	where K_t is the intraparticle diffusion rate constant (mg/g min1/2) and C is a constant that gives an idea about the thickness of the boundary layer effect (mg/g)		

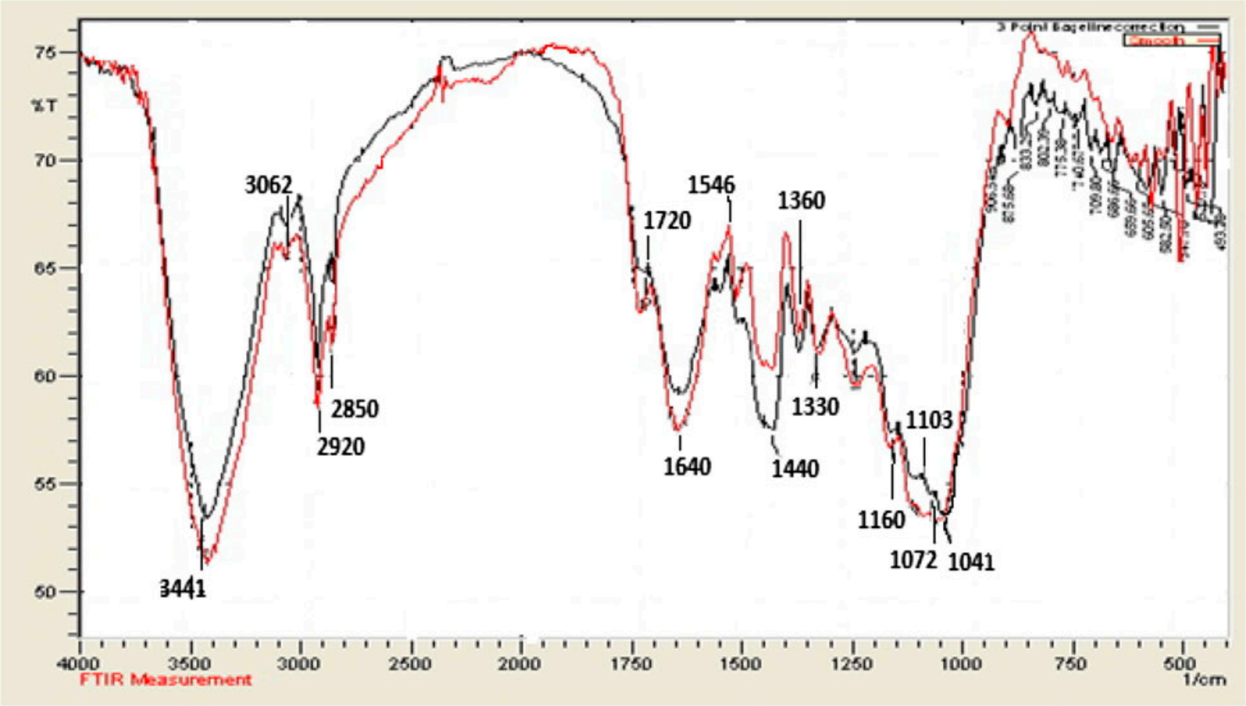

Fig. 2. FTIR spectra of raw (black line) and Pb(II)-loaded (red line) SBTL.

number of functional groups. These results are in agreement with those reported by Arief et al. [26], who noted that the adsorption capacity of Cr(VI) was strongly influenced by type and number of functional groups on the surface of the biosorbent.

3.2. Effect of pH

The efficiency of the sorption process is pH dependent owing to the fact that the variation in the pH value leads to difference in the surface properties of the biosorbent and degree of ionization [28]. In this study, the effect of pH in the range from 2 to 7 on the Pb(II) biosorption efficiency were studied, and the results are depicted in Fig. 3(a). The results showed that the solution pH played a significant role in the Pb (II) biosorption process onto SBTL. It can be observed from Fig. 3(a) that at pH between 2 and 3, the removal efficiency was low; however, with an increase in the pH to 5, the removal efficiency rapidly increased. It is worth mentioning that at a pH value of 5, almost 91% of the initial Pb(II) content was removed by SBTL. This phenomenon can be explained by the surface charge of the biosorbent active sites, and the H^+ ions present in the solution. At a lower pH, the active surface sites of the SBTL were either positively charged, causing the protons to compete with the metal ions [29], or dissociated [30], which resulted in a decrease in the Pb(II) removal efficiency. At a pH range from 5 to 7, the removal percentage was decreased because some active groups on the SBTL surface may be less protonated according to the zeta potential [31].

3.3. Effect of temperature

The variation in temperature has two major effects on the sorption process. Increasing the temperature is known to increase the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particles as a result of reduced viscosity of the solution [15]. In this study, the temperature effect on the Pb(II) removal efficiency was investigated within a temperature range of 15–55°C and the results are depicted in Fig. 3(b). It can be seen from the figure that the maximum percentage of heavy metal removal occurred between 25

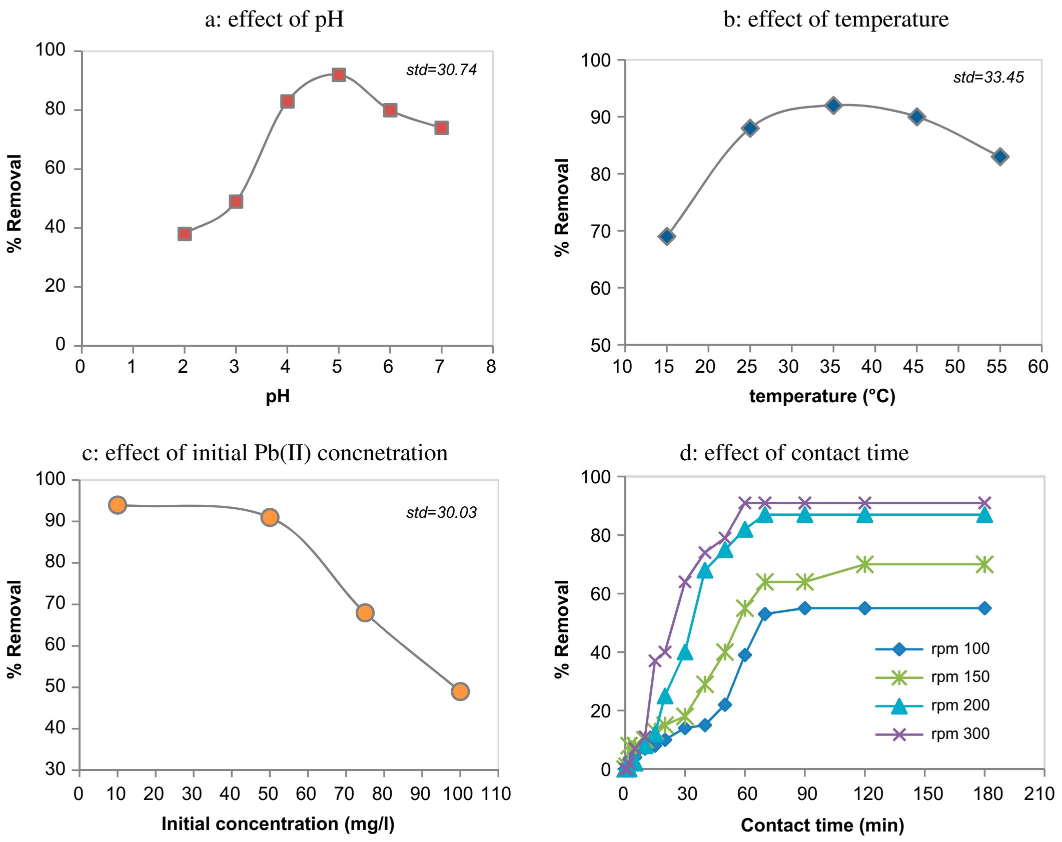

Fig. 3. Effect of experimental conditions on Pb(II) removal efficiency.

and 45˚C. Several authors have shown that further increases in the temperature lead to a decrease in the percentage of metal removal. This may be attributed to an increase in the relative desorption of the metal from the solid phase to the liquid phase, deactivation of the biosorbent surface, destruction of active sites on the biosorbent surface owing to bond disruption [32,33], or weakness of the sorbent active site binding forces and sorbate species and also between the adjacent molecules of the sorbed phase [34]. Moreover, as shown in Fig. 3(b), the variation in the temperature from 25 to 35˚C had minimal effect on the biosorption process; hence, all the biosorption experiments can be conducted at room temperature without adjustment.

3.4. Effect of initial Pb(II) concentration

Fig. 3(c) shows the results of the experiments performed to determine the effect of the variation in the initial Pb(II) concentration on the metal removal percentage. The results indicated that the percentage removal of Pb(II) was slightly decreased with an increase in the initial Pb(II) concentration from 10 to 50 mg/l, whereas a rapid decrease in the percentage removal was observed at the initial concentrations between 50 and 100 mg/l. This behavior may be attributed to the decrease in the available sorption sites on the surface area of the biosorbent at a metal ion concentration from 50 to 100 mg/l. The same behavior had been observed in previous studies as well [35,36].

3.5. Effect of contact time

Fig. 3(d) presents the typical concentration decay curves of Pb(II) obtained at different rotation speeds. As shown in the figure, the metal removal efficiency increased with an increase in the rotation speed and remained constant after reaching equilibrium time. The optimum rotation speed needed to achieve maximum metal removal (91%) was 300 rpm. Pb(II) removal was rapid at the beginning of the first hour of contact time, and an equilibrium condition was gradually reached, which can be attributed to the high availability of surface binding sites on SBTL and the slow pore diffusion of the solute ions into the bulk of the adsorbent [25]. Vijayaraghavan and Yun [37] indicated that with appropriate rotation speed, the mass transfer resistance can be minimized. Their study showed that with the increasing rotation speed, the diffusion rate of a solute from the bulk liquid to the liquid boundary layer surrounding the particles becomes higher owing to the enhanced turbulence and decrease in the thickness of the liquid boundary layer. Therefore, in this study, the rotation speed was not increased above 300 rpm.

3.6. Biosorption isotherms

The biosorption isotherm is a plot that shows the amount of equilibrium uptake versus the concentration of the ion in the solution at equilibrium state [38]. In this study, the biosorption isotherm was obtained by measuring the equilibrium uptake at the initial Pb(II) concentration of 1–50 mg/l, as shown in Fig. 4. The biosorption capacity increased with the increase in the initial concentration of Pb(II) in the range of 1–40 mg/l, and then reached a plateau, and the static Pb(II) biosorption capacity (19.7 mg/g) of SBTL was obtained. It must be noted that several efforts have been taken to characterize the metal-binding properties of various forms of biomass. The uptake of metals by different biomasses is summarized in Table 3. It can be noted from the table that the SBTL has a low biosorption capacity, when compared with other biomasses, which may be owing to the fact that the other biomasses were treated or modified before use in the biosorption process.

Analysis of the isotherm data by adapting different isotherm models is an important step that can be used for design purpose [17]. The sorption isotherms can be modeled using numerous equations. However, the Langmuir and Freundlich equations are the most frequently used when considering metal sorption processes. The linearized form of these two equations is presented in Table 2. A plot of (C_e/q_e) versus C_e should yield a straight line if the Langmuir equation is obeyed by the sorption equilibrium. The slope and intercept of this line yield the values of constants q_m and K_L, respectively. The Freundlich coefficients can be determined from the plot of ln q_e versus ln C_e. Table 4 shows the resultant constants of the Langmuir and Freundlich isotherms. The isotherm data fitted well the Freundlich model than the Langmuir model. The good fit of the experimental data by the Freundlich equation confirms that the sorbent material can be considered for heterogeneous sorbtion.

3.7. Kinetic study

Many applications such as wastewater treatment and metals purification require rapid sorption rate and short contact time. The sorption rate is an important parameter used to image the sorption process [39]. The kinetics of metal ion biosorption determines the rate as well as simultaneously calculates the residence time in

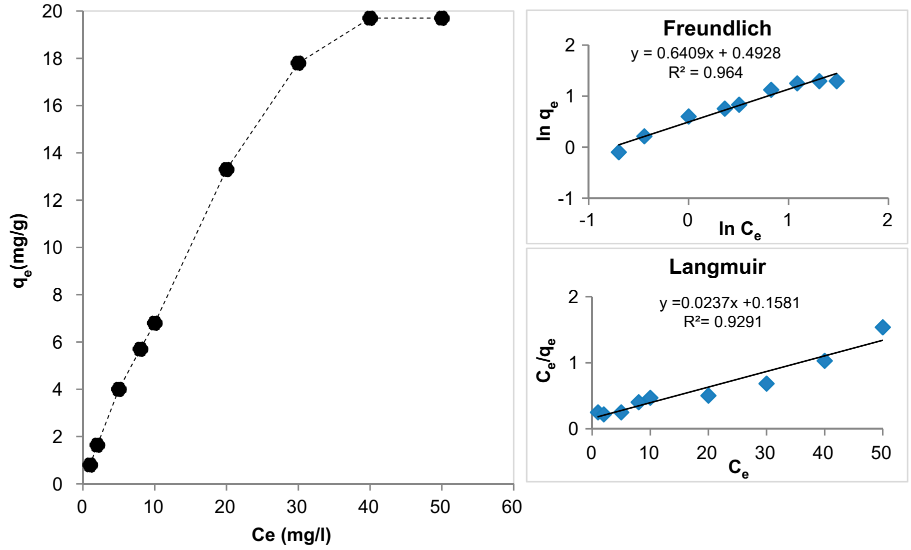

Fig. 4. Isotherm results for Pb(II) biosorption using SBTL: Pb(II) concentration = 1–50 mg/l, contact time = 3 h, rotation speed = 200 rpm, pH 5, SBTL dose = 1 g, temperature = room temperature, std = 7.31.

Table 3
Uptake of Pb(II) by different biomasses

Biomass	q_e (mg/g)	Reference
Spent leaves of green and black tea	83.00	[10]
Dead anaerobic biomass	54.92	[44]
Barley husk	12.70	[45]
Alkali treated tea residue	64.10	[46]
Spent black tea leaves	19.7	This study

Table 4
Langmuir and Freundlich isotherm constants for the biosorption of Pb(II) onto SBTL

Langmuir isotherm model	Freundlich isotherm model
$n = 1.56$ g/l	$q_m = 42.19$ mg/g
$k_f = 3.11$ mg/g	$k_L = 0.15$ 1/mg
$R^2 = 0.964$	$R^2 = 0.929$

batch/continuous mode operations and efficiency of a sorbent [40]. The kinetic process is mainly affected by the particle sizes of the sorbent in the initial stage of the biosorption. A decrease in the size of the sorbent particles increases the contact surface between the particles and solution. However, the size of the sorbent particles may affect the resistance to intraparticle diffusion by increasing the diffusion length to the center of the particles [41]. Fig. 5 shows the time dependence of the Pb(II) sorption capacity of SBTL. It can be seen that the sorption capacity of Pb(II) increased with time during the first hour and then reached saturation. This fast sorption process could be owing to the strong chelation of the biosorbent and its smaller diffusion barrier [37,38].

Three different kinetic models (pseudo-first-order, pseudo-second-order, and intraparticle diffusion kinetic models) were used in this study to fit the experimental data. The linear expression of these models is presented in Table 2. The rate constant k_1 (1/min) and correlation coefficients of the first-order-model were calculated from the linear plot of ln (q_e−q_t) versus t, and are listed in Table 5. The second-order-kinetic model is based on assumption that the sorption follows second-order chemisorption [21]. The rate constant of the pseudo-second-order sorption k_2 (g/mg min) was calculated from the linear plots of t/q_t versus t and is given in Table 5. According to the intraparticle diffusion model, the plot of q_t versus $t^{1/2}$ should be a straight line. When $C < 0$ or the plot does not pass through the origin, it indicates some degree

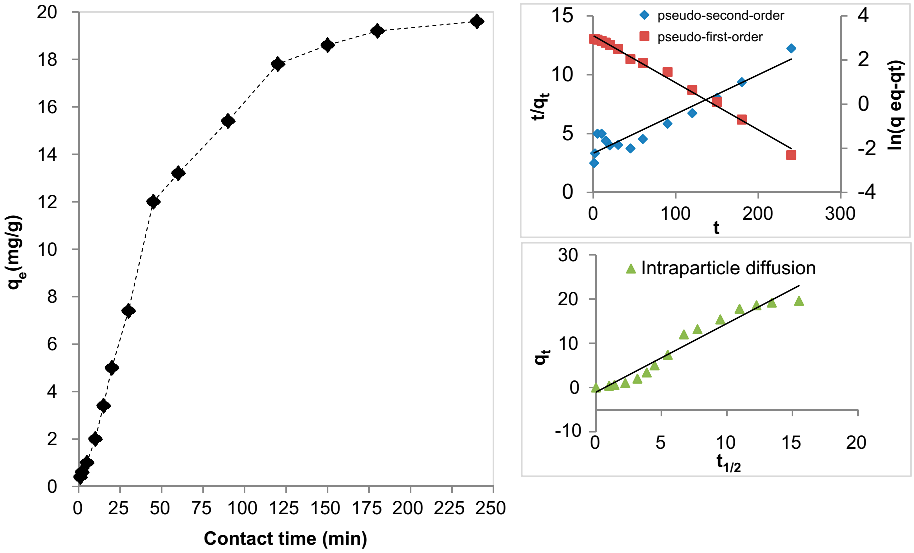

Fig. 5. Kinetic results for Pb(II) biosorption using SBTL: Pb(II) concentration = 1–50 mg/l, contact time = 3 h, rotation speed = 200 rpm, pH 5, SBTL dose = 10 g, temperature = room temperature, std = 7.64.

of boundary layer control. In addition, this observation further shows that the intraparticle diffusion is not the rate-limiting step, and other kinetic models may also control the rate of sorption [42,43].

A straight line with high correlation coefficients ($R^2 > 0.99$) was obtained for the first-order-kinetic model. For the second-order model, a large deviation between the calculated values and the experimental values of sorption capacity was noted. These results suggest that the first-order-kinetic model can be successfully used to describe the kinetic of the biosorption of Pb(II) onto SBTL.

3.8. Biosorptive-flotation experiments

The biosorption batch study revealed that the contact time of SBTL for >90% removal of Pb(II) was 60 min. Subsequently, flotation process was conducted for 15 min, and the results are depicted in Fig. 6. It can be noted that the flotation process increased the Pb(II) removal percentage from 91 to 98%. Fig. 7 shows the results of turbidity studies (NTU). It can be noted from the figure that a rapid separation of SBTL biomass from 80 to 7 NTU was achieved within the first 10 min. This is a specific advantage of the proposed biosorptive-flotation process, because it is highly effective not only concerning Pb(II) removal, but also owing to the fact that the subsequent biomass separation process from the solution is fast and relatively cheap due to the requirement of less residence time. Furthermore, the effect of gas flow rate (500, 1,000, and 1,500 ml/min) on the removal efficiency of Pb(II) in the bubble column was investigated, as shown in Fig. 8. It can be observed from the figure that the removal rate was highly affected by the gas flow rate. An increase in the gas flow rate from 500 to 1,000 ml/min led to an increase in the removal rate by about 3% after 15 min of operation. However, in the biosorptive-flotation system, the removal rate increased to 99% when the gas flow rate was increased to 1,500 ml/min. The increase in gas flow rate also increased the removal ratio because the increased gas flow rate caused early bubble detachment, prominent fluid activities (stress) at the bottom

Table 5
Kinetic parameters of Pb(II) biosorption onto SBTL

q_{eq} (exp) (mg/g)	Pseudo-first-order model			Pseudo-second-order model			Intraparticle diffusion model		
	k_1 (1/min)	q_{eq} (cal.) (mg/g)	R^2	k_2 (g/mg min)	q_{eq} (cal.) (mg/g)	R^2	K_t (mg/g min$^{1/2}$)	C (mg/g)	R^2
19.7	0.0213	22.2	0.993	0.0037	30.03	0.908	1.554	−1.08	0.9512

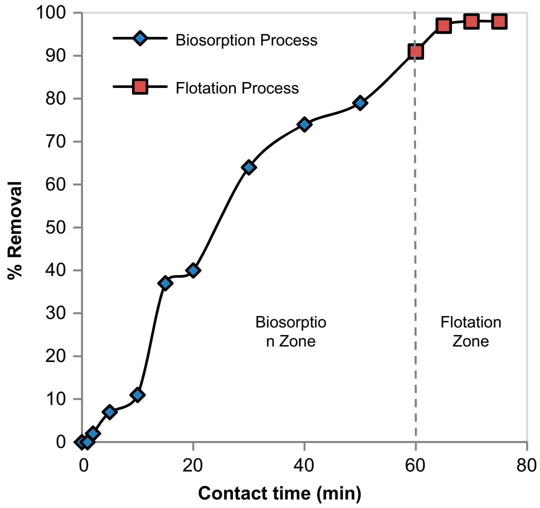

Fig. 6. Effect of the flotation process on the removal efficiency of Pb(II) using SBTL.

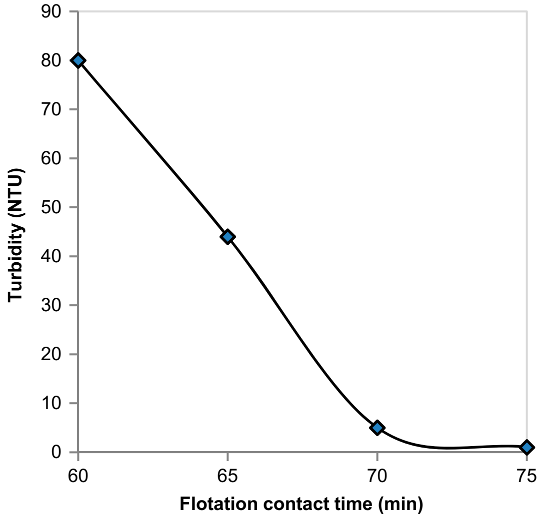

Fig. 7. Effluent turbidity concentration.

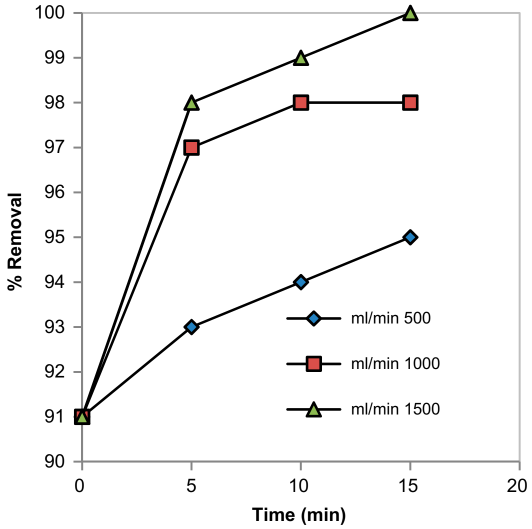

Fig. 8. Effect of gas flow rate on the Pb(II) removal efficiency ($C_0 = 50$ mg/l; pH 5; SDS = 50 mg/l; SBTL = 20 g/l).

section, and bubble coalescence and (mostly) breakup. This led to a large number of small bubbles, which increased the surface area available for adsorption by metal collector [47]. However, higher gas flow rate resulted in a decrease in the removal rate from the maximum owing to the dispersion of some of the metal collector and precipitation of product back into the bulk solution; these results are in agreement with those reported earlier [45].

To determine an optimal concentration of SDS for removing Pb(II) ions from aqueous solutions, a series of experiment was conducted using different concentrations of SDS (25, 50, and 100 mg/l). The results obtained are presented in Fig. 9. The removal of Pb(II) reached a maximum value when the concentration of SDS was 50 mg/L. An increase in the SDS concentration from 25 to 50 mg/l had a reasonable effect on the removal rates, which were 92 and 98%, respectively, while a further increase in the SDS concentration from 50 to 100 mg/l led to a decrease in the removal rate from 98 to 96% after 15 min of operation. Higher concentrations of the surfactant (100 mg/l) impaired flotation, and poor flotation at high surfactant

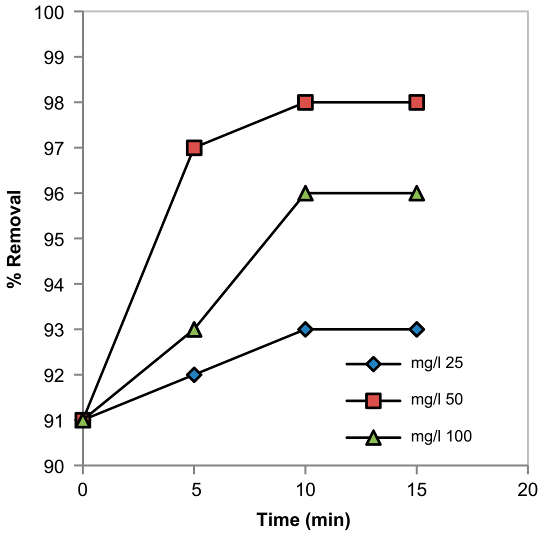

Fig. 9. Effect of SDS concentration on the Pb(II) removal efficiency ($C_0 = 50$ mg/l; pH 5; gas flow rate = 1,000 ml/l; SBTL = 20 g/l).

concentration caused the formation of air bubbles on the surface of the stable, hydrated envelope of the surfactant, or, perhaps, resulted in the formation of a hydrated micelle coating on the solid surface. Consequently, the resulting hydrophobic surface was not suitable for flotation. These findings are in agreement with those reported by Matis et al. [13].

4. Conclusions

This study assessed the feasibility of Pb(II) biosorption using SBTL, which is a natural and abundant material. This biosorbent showed good affinity for Pb (II), and the maximum uptake was 19.7 mg/g. FTIR analysis showed that the biosorption was a complex process and depended on the number and type of active groups, and carboxyl, amino, and sulfonic groups were noted to be involved in this process. The isotherm data indicated that Freundlich model provided better correlation of experimental data. The modeling of kinetics data showed that the biosorption profile can be described by the first-order-kinetic model, suggesting that the biosorption process is presumably a physical sorption. The maximum percentage removal obtained under optimum conditions in the batch system was 91%, which was increased to 99% by using flotation system. Finally, analysis of effluent turbidity of the flotation system showed that after 15 min of contact time, the turbidity was decreased to negligible values.

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