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Original Research

Bioremoval of Tl (I) by PVA-Immobilized Sulfate-Reducing Bacteria

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Abstract

As scattered elements, thallium (Tl) contamination poses a significant threat to human health due its high toxicity. Sulfate-reducing bacteria (SRB) embedded in PVA-sodium alginate matrix was utilized as a novel bio-remover to remove Tl from aqueous solution. The effect of pH, temperature, and initial Tl concentration on removal capacity of immobilized beads were studied and discussed in this work. The optimum bio-removal conditions were at pH value of 6, temperature of 35ºC, and initial Tl concentration of 50 $mg.L^{-1}$. The pseudo second-order model for Tl adsorption was applicable to all the removal data over the entire time range and intralayer diffusion was not the only rate-determining step. The bio-removal data conformed well to Langmuir isotherm model. Fourier transform infrared spectroscopy showed that sulfate reduction played an important role in Tl removal. The groups of carboxylate radical might be involved in sulfate reduction reaction.

Keywords: immobilized cells, sulfate-reducing bacteria, thallium, aqueous solution

Introduction

Thallium (Tl) and its compounds have been widely used in many respects of human life, including for medical purposes, imitation jewelry, low-temperature thermometers, ceramic semiconductor material, fireworks, and pigments [1]. As one of the 13 priority pollutant metals, Tl was reported to be more toxic to human health than mercury, cadmium, lead, copper, or zinc [2]. It was a quite mobile metal and readily transported through aqueous routes into the environment due to the high solubility of its compounds. Tl was well known to have been responsible for many accidental, occupational, and therapeutic poisonings [3]. Its discharge and bioaccumulation in the environment has led to serious threats to human health or even causing death via drinking water and consuming vegetables, domestic birds, and animals bred in a Tl-polluted area, and inhaling Tl-bearing particles [4].

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Concentrations in Tl-bearing wastewater have been observed to range from 1 to 1,600 μg.L^{-1} of Tl. Considering its high environmental toxicity and undoubted risks to human health, Tl-bearing wastewater with Tl concentrations above 2 μg.L^{-1} have required being treated if discharged into surface water identified as a drinking water source [5-7]. Generally, Tl-bearing wastewater was treated with adsorption, oxidative precipitation, ion exchange, filtration, electrodialysis, and reverse osmosis for decontamination [7-9]. However, these processes were expensive and complex facilities or they led to secondary pollution [6]. For example, ion exchange was easily affected by environmental factors. Reverse osmosis was also an energy-condensed process. The restoration of membranes was hard after Tl removal [10]. Meanwhile, Tl-bearing wastewater usually was accompanied by high sulfate concentrations, which would affect the adsorption effect of activated alumina.

The bio-removal method was supposed to be a promising approach for heavy metal-bearing wastewater treatment. It was an economical and environmentally friendly approach since various natural materials, including bacteria, fungi, yeast, algae, etc., were utilized in the biosorption process [11-12]. Furthermore, the bio-removal process was able to remove Tl in dilute complex wastewaters from ppm to ppb level, which was suitable for treating Tl-polluted low-concentration complex solutions in a large scale, which was suitable for controlling the pollution of scattered elements in aqueous solution [13]. As a group of morphologically diverse and anaerobic microorganisms, sulfate-reducing bacteria (SRB) was a promising alternative to the traditional heavy metal remediation method. Sulfate was used as the terminal electron acceptor to produce hydrogen sulfide. Therefore, hydrogen sulfide was a promising option for achieving simultaneous removal of heavy metals and reduction of sulfate from wastewater through precipitation with heavy metals, especially Cu, Zn, and Fe [14]. Tl toxicity in the aqueous phase could be reduced through these mechanisms of SRB. The biological transformation process is described in Eqs. (1-2) [15].

$$2CH_2O+SO_4^{2-}\rightarrow H_2S+2HCO_3^- \quad (1)$$

$$H_2S+Tl^+\rightarrow Tl_2S_{(s)}+2H^+ \quad (2)$$

…where CH_2O represents the electron donor. However, ordinary anaerobic sludge existed several shortcomings of loosing floc structure, poor sedimentation performance, less unit microbial content, low activity, and bacterial species loss vulnerable to environmental factors, such as pH value and temperature [16].

Biological immobilization approaches had attracted great attention due to its high stability, high reactivity, and high processing efficiency [17-19]. Immobilized microspheres provided a suitable micro-environment for the SRB. It was reported that metal toxicity was controlled by immobilized SRB with strong resistance to metal ions by Min and Chai [20]. It was an ascendant technique that could be employed to remove high toxicity of heavy metals from aqueous solution. Sulfate-reducing bacteria immobilized on a fibrous slag (FS) was employed to recover cadmium through sulfide precipitates from low concentrations of cadmium-bearing water and, finally, the total amount of cadmium sulfide recovered 27.3 mg per unit gram of FS [21]. The application of PVA in immobilizing SRB has received considerable attention due to its non-toxicity and low-cost properties compared with other supporting materials. PVA-immobilized SRB could enhance heavy metal removal and the resistance of SRB to heavy metal toxicity [22]. PVA-immobilized SRB granular removed up to 94.13% of sulfate, and up to 84.39% of manganese and ferrous ion in the process of treating synthetic acid mine drainage after five days[23]. PVA-immobilized SRB lowered leaching toxicity and achieved removal efficiencies of 76.3%, 95.6%, 100%, and 91.2% for Cu, Zn, Pb, and Cd, respectively [24]. However, no studies have been carried out to investigate the application of PVA-immobilized SRB for Tl removal. The kinetics and isotherm model of Tl-polluted wastewater treatment through immobilized SRB have never been investigated.

The objective of this study was to investigate Tl bio-removal by PVA-immobilized SRB. The effect of pH value, temperature, and sulfate concentration of aqueous phase on Tl removal have been investigated in detail. The kinetics and mechanism of Tl removal by PVA-immobilized SRB was also studied thoroughly. The immobilized beads of SRB were characterized by fourier transform infrared (FTIR) spectroscopy to discuss the possible removal mechanism of PVA-immobilized SRB.

Materials and Methods

Bacterial Source of SRB

The SRB strain was isolated from an up-flow anaerobic sludge bed (UASB) which was used directly to treat acid mine drainage. The raw sludge was filtered and then fed with culture medium to form a mixture with 2% sludge. The culture medium was composed of (per liter of deionized water): 2.0 g $MgSO_4$, 1.5 g KH_2PO_4, 0.1g NH_4Cl, 0.5g cysteine hydrochloride, 0.5 $(NH_4)_2Fe(SO_4)_2.6H_2O$, 1 g yeast extract, 0.1 g $CaCl_2$, 0.3 g sodium citrate, 0.1 g ascorbic acid, and 2.0 g sodium lactate. The pH of the medium was adjusted to 7.0±0.1 by 0.01 M HCl and 0.01 M NaOH. The mixture was placed in a 250 ml anaerobic flask and charged with nitrogen gas for 10 min to remove dissolved oxygen (DO). Then it was sealed and transferred into an anaerobic workstation (YQX-II, Yuejing, China) for enrichment. 1 mL culture mixture was inoculated into the next flask with 100 mL culture solution. This step was repeated three times. The enrichment culture was diluted into different gradient concentrations and inoculated on solid culture medium with the above reagents by conventional spread plate techniques in anaerobic workstations for 48 h. Black colonies were picked and

then purified three times by streak dilution plating. When colonies growing on plates had the same appearance, they were collected and inoculated into another anaerobic flask with 100 mL culture solution for 48 h enrichment. The bacteria were collected and used for preparing PVA-immobilized SRB beads. All incubations were done at 30ºC in the dark. Stock cultures were stored at 4ºC and regularly transferred to fresh medium to maintain viability.

Preparation of PVA-Immobilized SRB Beads

Immobilization of biomass via entrapment was carried out as follows: the polyvinyl alcohol solution (6%, w/v), silica solution (3%, w/v), and sodium alginate solution (0.5%, w/v) were dissolved in deionized water and mixed thoroughly. Activated carbon solution (1%, w/v) and SRB suspended solution (35%, w/v) were added into the colloid and mixed evenly at 40ºC. The alginate-biomass mixture was then extruded through a 10 ml syringe into a 100 ml $CaCl_2$ (1%, w/v) solution for polymerization. Each gram of the beads contained an average of 0.15 mg of bacteria. The average diameter of the beads was approximate 2 mm. Finally, immobilized beads were rinsed twice with sterile saline and stored at 4ºC for further use [25].

Chemicals

The PVA (with 99.4-99.8% saponification), NaCl, sodium alginate, and SiO_2 used in this study were supplied by Damao chemical reagent factory (analytical grade, Tianjin, China). A filter-sterilized solution of $TlNO_3$ (Guangdong Analysis and Testing Center, AR grade) was used as a source of Tl(I). 0.45 μm microporous membrane filters were supplied by Laboratory Equipment Co., Ltd, China. All other chemicals used in this study were supplied by Zhiyuan Chemical Reagent Factory (analytical grade, Tianjin, China).

Bio-Removal Experiments

A series of experiments with variations of reaction conditions were conducted to investigate the effects of pH value, initial thallium concentration, and contact time, together with thermodynamics and kinetic studies on the Tl biosorption process.

Effect of temperature on Tl removal by the beads had been studied by using seven sets with three flasks for each set. These flasks were also autoclaved with 1 g beads (wet weight) being added into each flask containing 100 ml of Tl-bearing solution. The original pH values were adjusted from 2.0, 3.0, 4.0, 5.0, 6.0, and 7.0 to 8.0 with 0.01 M HCl and 0.01 M NaOH. All experiments were conducted at reaction temperature of 35ºC, 150 rpm, initial Tl concentration of 20 mg L^{-1}, and contact time of 24 h. The temperature of the solution was controlled by shaking Baths (Jintan, SHZ-88, China).

In order to study the effect of initial Tl ion concentration and temperature on biosorption, together with thermodynamics and kinetic studies, experiments were conducted with various initial thallium ion concentrations from 1 to 100 mg L^{-1} at different temperatures of 30ºC, 35ºC, and 40ºC, 150 rpm and the pH value was adjusted to 7 by 0.01M NaOH or 0.01M HCl. These flasks were also autoclaved with 1g beads (wd) being added into each flask containing 100 ml of different concentrations of Tl-bearing solution.

Two ml of samples from reaction were periodically collected after 24 h shaking. Samples were filtered with 0.45 μm microporous membrane filters to estimate Tl concentration in the medium. Each Tl biosorption test was replicated three times, and the mean value and standard error were calculated to obtain reliable data. Tl concentration was determined using the flame atomic absorption method with a flame atomic absorption spectrometer (FAAS, TAS990, Beijing, China) [26].

Metal uptake capacity q (mg.g^{-1}) was calculated by the following mass balance equation:

$$q = \frac{(C_0 - C_i)\ V}{m} \quad (3)$$

…where C_0 was the initial Tl concentration ($mg.g^{-1}$), C_i was the Tl concentration at equilibrium ($mg.g^{-1}$), V was the volume of solution (L), and m was the weight of immobilized SRB (g).

FTIR Analysis of Biomass

Beads were dried at 40ºC, then grounded and sieved through a 200 mesh sieve for FTIR spectroscopy analysis (Tensor27, Bruker, Germany) equipped with a KBr beam splitter and a DTGS detector. Spectra of immobilized beads in absorbance mode between 4,000 and 400 cm^{-1} was recorded [27]. Background spectrum was recorded on a clean ZnSe spectral window.

Results and Discussion

Effect of pH on Tl Removal

In this work, pH values were varied to study the effect of pH value on biosorption of Tl. As shown in Fig. 1, Tl removal capacity increased from 118.77 to 229.92 mg g^{-1} bacteria when pH value increased from 2.0 to 6.0, then it decreased from 226.47 to 211.88 mg g^{-1} bacteria when pH value further increased from 7.0 to 8.0 (Fig. 1). pH value played an important role in the bioremoval of heavy metal from aqueous solution. Hydrogen ions can vigorously compete with Tl(I) for the adsorption sites and the bacteria activity would be suppressed by low pH [28]. In addition, low pH value was not suitable for bacteria production and thus may cause a decline in metals adsorption. Along with the increase in pH value, Tl removal capacity gradually increased due to the increasing bacteria activity at a more adequate pH condition. However, high pH value was unfavorable for the growth of SRB since most SRB thrived at an optimum pH, ranging from 6.0 to 7.0 [29]. In

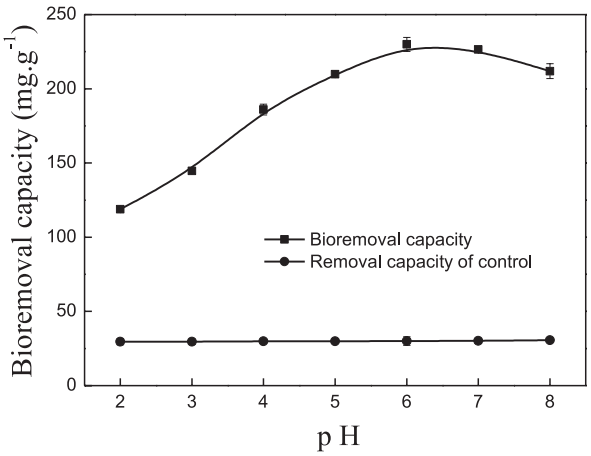

Fig. 1. Bioremoval capacity of Tl(I) at different pH. Control was blank beads without cells. All experiments were performed in triplicate. Bars represent standard deviation.

our study, the optimum pH for Tl removal was around 6.0. The higher pH value led to a decrease in Tl removal, which was in line with the findings previously reported by Singh et al. [29-30]. Therefore, a pH value of 6 was suitable for Tl removal by the PVA-immobilized SRB beads.

Effect of Initial Tl Concentration and Temperature on Tl Removal

According to Fig. 2, when the initial Tl concentration increased from 25 to 50 mg L^{-1}, the bio-removal capacity of Tl increased to 182.07, 221.34, and 207.91 mg g^{-1} at 30ºC, 35ºC, and 40ºC, respectively. However, it is shown that Tl removal reached a plateau when initial Tl concentration increased to 100 mg g^{-1} (Fig. 2). Concentration difference is a driving force to overcome the mass transfer resistance between liquid and solid stages, leading to a higher Tl removal capacity at a larger initial Tl concentration. Tl ions may have more chances to

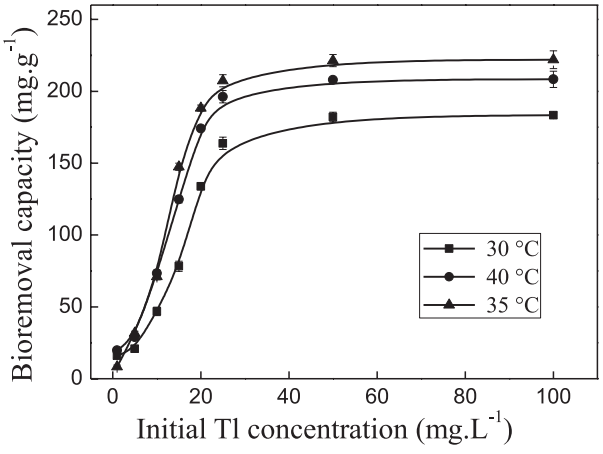

Fig. 2. Bioremoval capacity of Tl(I) at different initial Tl concentration and temperature. All experiments were performed in triplicate. Bars represent standard deviation.

contact with adsorption sites when initial Tl concentration progressively increased. After full occupation of the active sites, Tl removal reached a peak level and did not increase when higher initial Tl concentration was used. It should be noted that hydrogen sulfide produced by the SRB could react with Tl(I) to form Tl_2S precipitate, which was favorable to Tl removal [15]. On the other hand, a high initial Tl concentration to an inhibitory level would restrain the activity of the SRB. In this study, the SRB were inhibited at the initial Tl concentration higher than 50 mg/L, suggesting that the highest initial concentration of Tl should not be higher than this value.

As presented in Fig. 2, a higher removal capacity was observed at 35ºC than at 30ºC and 40ºC. The higher the temperature, the more active sites presented in immobilized beads due to the enhanced protonation and depronation rate of functional groups at higher temperature [31]. However, the activity of bacteria was slightly reduced at 40ºC, suggesting that the optimum temperature of this bacterial strain is 35ºC. This finding is in line with other studies in which the optimum growth temperature of most mesophilic SRB was reported in the range of 28-38ºC [32]. Therefore, the optimum initial Tl concentration and temperature were 50.0 mg L^{-1} and 35ºC for Tl removal from the aqueous solution by PVA-immobilized SRB.

Bio-Removal Kinetic Studies

Lagergren pseudo first-order (LPFO), Lagergren pseudo second-order (LPSO), and intraparticle diffusion model (IPD) were employed to model the sorption data over the entire time range. Relevant equations are generally expressed as [33]:

(1) LPFO:

$$\ln (q_e - q_t) = \ln q_e - k_1 t \quad (4)$$

(2) LPSO:

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

The correlation coefficient (R^2) and average absolute percentage deviation (D%) were applied to assess the kinetic mechanism of biosorption [34]. The D percentage values can be computed as:

$$D\% = \frac{1}{N}\sum_{i=1}^{N}\left|\frac{q_{e.exp} - q_{e.cal}}{q_{e.exp}}\right| \times 100 \quad (6)$$

(3)IPD:

$$q_t = k_3 t^{1/2} + C \quad (7)$$

…where q_e and q_t are the adsorption capacity (mg g^{-1}) at equilibrium and time t, respectively; k_1 is LPFO rate constant (min^{-1}); k_2 is LPSO rate constant (mg $g^{-1}min^{-1/2}$); k_3 is IPD rate constant (mg $g^{-1}min^{-1/2}$); $q_{e.cal}$ is the removal

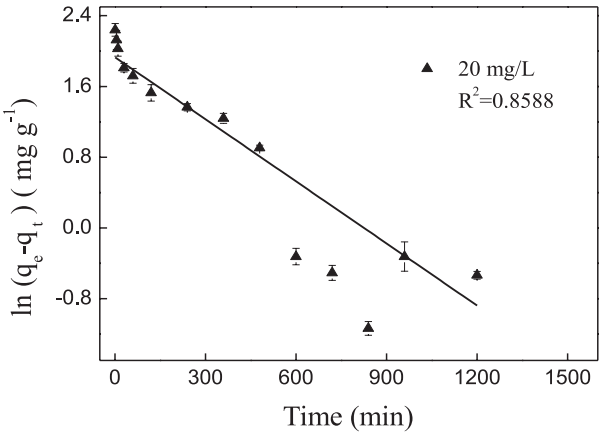

Fig. 3. Plot of $\ln(q_e-q_t)$ vs. t.

equilibrium capacity (mg.g^{-1}); $q_{e.exp}$ is the actual capacity of removal equilibrium (mg g^{-1}); N is the number of removal; and C is a constant.

Plotting to $\ln(q_e-q_t)$ versus time t, t/q_t versus time t and q_t versus time $t^{1/2}$, respectively (Figs 3-5). The kinetic parameters were calculated by the slope and intercept of the fitting equation (Table 1). Fig. 3 shows the plot of $\ln(q_e-q_t)$ versus time t. The relationship was not linear over the entire time range (R^2 = 0.8588), indicating that more than one mechanism is related in bio-removal. At the same time, LPSO had a higher R^2 and lower D%, which indicated that the LPSO model fit better to the experiment data than LPFO (Table 1).

Meanwhile, $q_{e.cal}$ was closer to $q_{e.exp}$ in LPSO than in LPFO, which confirmed that there were several mechanisms involved in the removal process [35].

The adsorption process can be divided into three phases: namely the film diffusion stage, the intralayer diffusion stage, and the dynamic equilibrium stage [36]. Generally, total removal rate was controlled by film diffusion, intralayer diffusion, or both. The kinetic data were fit with IPD in order to further study the bio-removal mechanism of immobilized SRB for Tl removal (Fig. 5a).

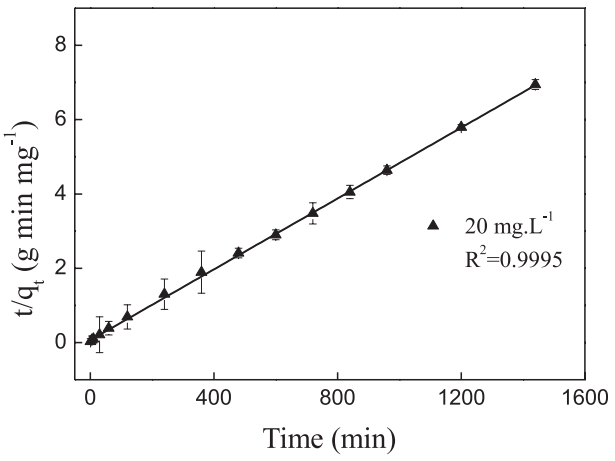

Fig. 4. Plot of t/q vs. t.

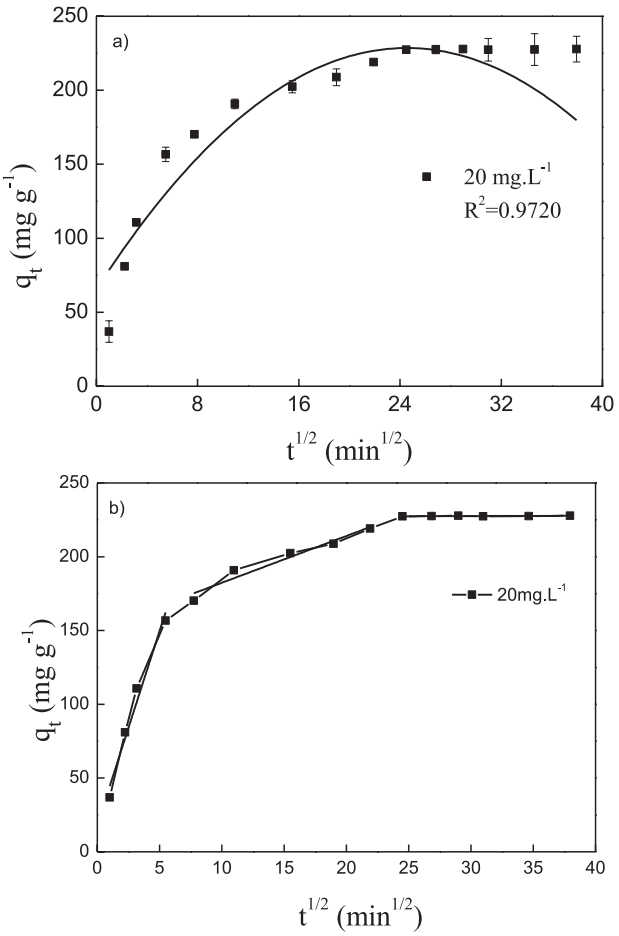

Fig. 5. Plot of q_t: a) curve fitting, b) linear fitting.

The relationship between q_t and $t^{1/2}$ was not linear over the whole time range, which indicated that there were several processes affecting bio-removal. The effect of film diffusion of the rate-determining step was also great according to Weber [37] (Fig. 5b).

Theoretically, if the intra-particle diffusion was the only rate-determining step, the initial rate parameter (k_3) should be directly related to constant C. However, in this study the k_3 was far less than C (Table 1), which confirmed that intra-particle diffusion was not the only rate-determining step for Tl bio-removal by immobilized SRB.

Bio-Removal Isotherm Model Studies

The bio-removal isotherms indicated the reaction pathway of how adsorbents interact with adsorbates, which was described by Langmuir and Freundlich adsorption isotherms, respectively. Isotherm experimental studies were conducted with various initial Tl ion concentrations from 1 to 100 mg.L^{-1} and analyzed by Freundlich and Langmuir isotherm models at different temperatures of 30, 35, and 40ºC. The correlation regression coefficients and constants of Tl biosorption are presented in Table 2.

Table 1. Kinetic Parameters of LPFO, LPSO, and IPD for Tl removal by immobilized SRB at fixed pH value of 7 with buffer solution at 35ºC.

Equation	$q_{e.exp}$ (mg g^{-1})	$q_{e.cal}$ (mg g^{-1})	K_1 (min^{-1})	K_2 (mg $g^{-1}min^{-1/2}$)	R^2	K_3 (mg g^{-1} $min^{-1/2}$)	C (mg g^{-1})	D%
LPFO	207.3	8.2565	3.7×10^{-3}		0.8588	-	-	96.02
LPSO	207.3	212.77		3.6×10^{-4}	0.9995	-	-	2.64
IPD	207.3	-		-	0.9720	1.5116	13.2960	-

Table 2. Freundlich and Langmuir isotherm constants for Tl(I) adsorption on immobilized SRB at various temperatures.

T(ºC)	Freundlich model			Langmuir model			
	K_F	1/n	R^2	Q_m(mg g^{-1})	K_L(L mg^{-1})	R_L	R^2
30	15.08	0.6058	0.84	252.5253	0.03520	0.2212-0.9660	0.82
35	18.84	0.6134	0.86	259.7403	0.03423	0.2261-0.9669	0.90
40	11.18	0.7910	0.89	298.5075	0.02978	0.2514-0.9711	0.88

Freundlich Isotherm Model

The Freundlich isotherm model is an experimental model and generally described in the following equation [38]:

$$\ln Q_{eq} = \ln K_F + \frac{1}{n}\ln C_{eq} \quad (8)$$

…where Q_{eq} is the amount of Tl(I) ions adsorbed at equilibrium (mg.g^{-1}), C_{eq} is the equilibrium concentration of Tl ions (mg.L^{-1}) in the solution, and K_F and n are Freundlich constants related to the adsorption capacity and indication of favorability, respectively. As shown in Fig. 6a, the Freundlich isotherm model did not fit the experimental result well. K_F varied greatly with the increasing temperature (Table 2).

The adsorption intensity was favorable at higher temperature since all n values were greater than 1. However, the 1/n values below 1 indicated a normal Freundlich isotherm, which implied that the adsorption process was more heterogeneous as 1/n values gradually got closer to zero, while the 1/n values above 1 was a symbol of cooperation adsorption [39]. The 1/n values ranged from 0.61 to 0. 79 in the study (Table 2), which indicated that the adsorption process for Tl(I) ion adsorption on immobilized SRB was heterogeneous. As presented in Table 2, 35ºC was deemed the suitable temperature for Tl removal by the beads, which got higher K_F and lower 1/n values. Table 2 showed that the Freundlich isotherm model also satisfactorily fitted the sorption data at the temperature of 35ºC (R^2 = 0.86).

Langmuir Isotherm Model

The Langmuir isotherm model is a theoretical model for monolayer adsorption, which can be represented as [40]:

$$\frac{C_{eq}}{Q_{eq}} = \frac{1}{K_L Q_m} + \frac{1}{Q_m} C_{eq} \quad (9)$$

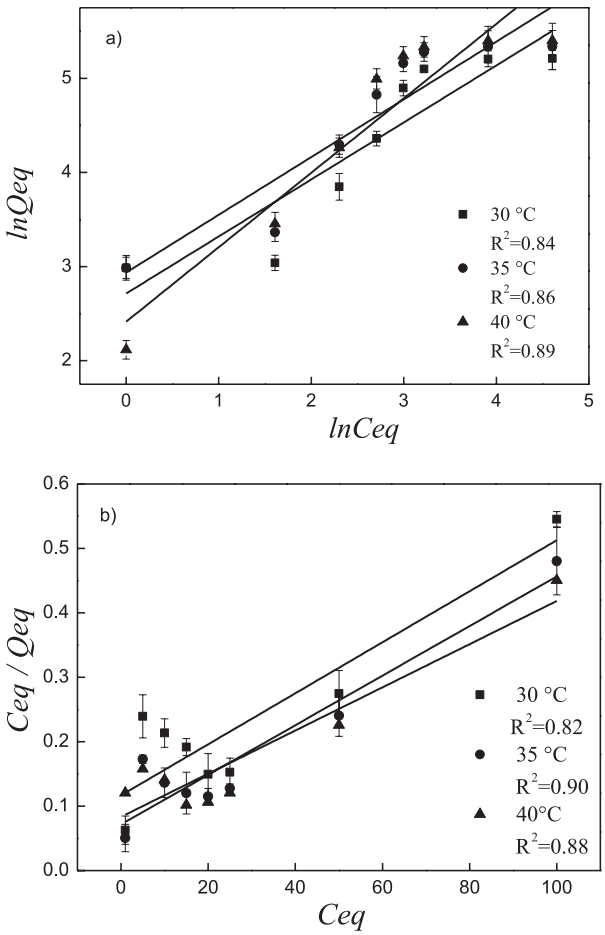

Fig. 6. Freundlich and Langmuir adsorption isotherm: a) Freundlich isotherm, b) Langmuir isotherm.

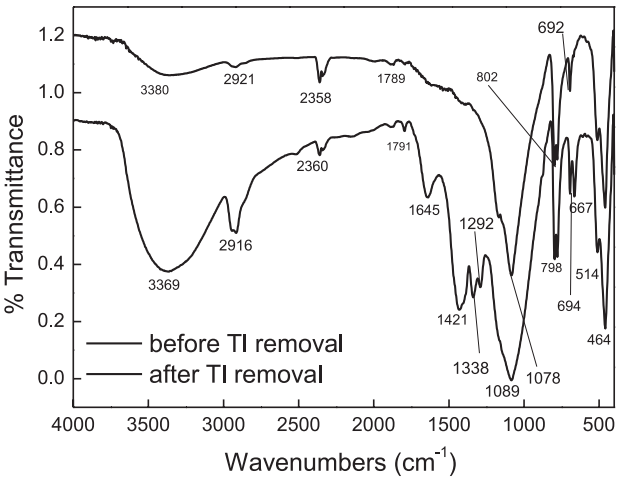

Fig. 7. FTIR spectra of immobilized beads.

$$R_L = \frac{1}{1 + K_L C_o} \quad (10)$$

…where Q_m is the maximum uptake capacity (mg g^{-1}), Q_{eq} is the amount of Tl(I) ions adsorbed at equilibrium ($mg.g^{-1}$), C_{eq} is the equilibrium concentration of Tl ions ($mg.L^{-1}$) in the solution, C_0 is the initial Tl concentration (mg L^{-1}), and K_L is the Langmuir adsorption intensity or coefficient related to the affinity between the binding sites of immobilized SRB and Tl(I) ions. R_L is the equilibrium index or a dimensionless constant separation factor that can be used to assess whether the adsorption process is favorable; other symbols are as previously described [41]. Compared with the Freundlich isotherm model, the Langmuir model was more fit Tl removal date well over a concentration of 1-100 $mg.L^{-1}$ (Table 2 and Fig. 6b). As represented in Table 2, 35ºC was the optimum temperature for Tl removal by the beads, the calculated Langmuir adsorption capacity, and the constant (K_L) at 35ºC was greater than the other temperatures.

FTIR Analysis of Immobilized Beads

FTIR analysis was used to characterize changes of functional groups before and after Tl bio-removal (Fig. 7). The intensity of the peak at 3,369 cm^{-1} was shifted to 3,380 cm^{-1} after Tl biosorption, which indicated that a hydrolysis reaction took place. The intensity of the peak shifted weakly from 2,916 to 2,921 cm^{-1} after bio-removal could be interpreted as the asymmetric and symmetric stretching vibrations of hydrocarbons in the immobilized SRB and partly bicarbonate radical disappearing. The intensity of the peak at 1,791 and 1,645 cm^{-1} turned weaker to 1,789 cm^{-1} may be interpreted as the carboxylate radical being affected by SRB [42]. The intensity of the peak at 1,089 cm^{-1} shifted to 1,078 cm^{-1}, and the intensity of the peak from 1,292 cm^{-1} to 1,421 cm^{-1} disappeared, which indicated that the stretching vibration of sulfate happened. The intensity of the peak from 464 cm^{-1} to 694 cm^{-1} transformed and parts of the peak disappeared, meaning that sulfate was reduced to sulfion by SRB, and sulfion would react with Tl(I) to form Tl_2S precipitation [43-44] (Fig. 7). Spectrum analysis of FTIR spectrum after Tl removal showed that sulfate reduction played an important role in Tl removal. The groups of carboxylate radical might be involved in sulfate reduction reaction.

Conclusions

In this work, SRB immobilized in PVA-sodium alginate matrix was utilized as a novel biological remover to remove Tl from aqueous solution. FTIR analysis was used to characterize changes of functional groups before and after Tl bio-removal. Sulfate reduction played key roles for Tl removal by PVA-immobilized SRB and the groups of carboxylate radical also might be involved in sulfate reduction reaction. The effect of pH value, temperature, and initial Tl concentration of the solution on Tl(I) removal process was investigated. The results proved that too high and too low pH value was not suitable for Tl removal by the beads of SRB and the suitable pH value was 6. Also, biosorption of Tl increased with the increasing initial Tl concentration when initial Tl content was below 50 $mg.L^{-1}$. The suitable bio-removal temperature was 35ºC. Tl(I) bio-removal by immobilized beads was well fitted by LPSO. The intra-particle diffusion was not the rate-determining step according to our removal kinetic analysis. The equilibrium of Tl biosorption was fairly well fitted by the Langmuir isotherm equation model.

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