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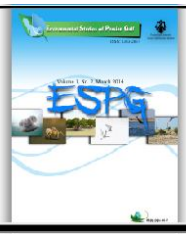

A Comparative Study of Two Indigenous Bacterial Biosorbents for Mercury Removal from Aqueous Solutions

Seyed Ali Jafari *, Sama Cheraghi

Department of Environment, Persian Gulf Research Institute, Persian Gulf University, Bushehr, Iran

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ABSTRACT

In the present study, the capability of dried indigenous biomass of *Vibrio* and *Oceanimonas*, was assessed and compared for mercury biosorption from aqueous solutions. It was found that both of the biosorbents reached equilibrium after 60 min of contact although the mercury sorption capacity of *Vibrio* was significantly more. Its sorption capacity increased from 9 to 83 mg/g biomass by increasing the initial metal concentration from 10 to 100 mg/L although the efficiency decreased from 90 to 83%. The changes in the pH of the medium had a great impact on the Hg^{2+} adsorption capacities of the bio sorbents. The maximum mercury bio sorption capacities were obtained under pH value of 6. The kinetic studies revealed that the pseudo-second order model described Hg^{2+} biosorption than the pseudo-firs order, for both of the bio sorbents better. The equilibrium isotherms showed that the Langmuir model described the mercury bio sorption by dried *Vibrio* better whereas the Freundlich was a dominant model for mercury bio sorption by *Oceanimonas*. According to the Langmuir model, the maximum mercury sorption capacities were achieved 193 and 113 mg/g biomass, respectively. Therefore, due to its high efficiency and high availability, the use of *Vibrio* as mercury biosorbent was a good alternative in mercury removal from water.

1 INTRODUCTION

The main portion of mercury pollutant in environment is from anthropogenic activities that include agriculture, battery production, fossil fuel burning, mining, and metallurgical processes (Green-Ruiz, 2006; Joo et al., 2010). In 2000, about 2190 tons of mercury was discharged into the environment as a result of these activities (Sinha et al., 2012). This element, which has been known as the most toxic heavy metals, can readily enter to live cell, accumulates in it, and disturbs its constructions (Green-Ruiz, 2006; Sinha et al., 2012). Upon entering the body, it attacks the neurons and causes a variety of neurological and physiological disorders (Bayramoğlu and Arıca, 2008). Therefore, finding a low-cost and appropriate technology to eliminate or reduce mercury concentration in environment has been the main concern of humans for many years.

Nowadays, the use of microbial approaches for heavy metal removal has received much attention. The low-cost operation, eco-friendly nature, and high efficiency especially at low

* *Corresponding author: sajafari.pgrsc@yahoo.com*

metal concentrations make this a promising process. Unlike the traditional physico-chemical techniques including chemical precipitation, ion-exchange resins, reverse osmosis, electro-chemical treatments, and evaporation are expensive and less efficient at low metal concentrations, and produce hazardous by-products (Joo et al., 2010; Sinha et al., 2012; Huang et al., 2013). The microbial techniques are divided into two main parts: The first is called bioremediation which uses metabolically active cells and the second is called biosorption which uses dead or inactivated cells. Dead cells have priority over living cells because there is no need to nutrition, easy metal desorption and contamination control is not required (Rezaee et al., 2006; Das et al., 2008; Plaza et al., 2011).

Bacteria, algae, fungi, and yeasts constitute a wide range of biosorbents with different adsorption capacities. These capacities depend on the cell wall structure and the affinity of surface ligands to specific metal ions. The detailed mechanisms of biosorption process have not been thoroughly studied due to the great variety of the biosorbents as well as complexity of the cell wall structure (Joo et al., 2010; Mo and Lian, 2011). Different parameters such as tendency toward the metal ions, the maximum sorption capacity, as well as the rate of the metal sorption on the surface of the biosorbents are the major criteria for comparing and choosing the best type of biosorbents for specific purposes. Using the equilibrium isotherms and kinetic studies are common for the calculation of these parameters. However, many factors including type of the metal ion, cell wall components of microorganisms, pH of the solution, temperature, ion strength, contact time, and the metal ion concentrations can influence the process efficiency and the quality of the biosorption (Joo et al., 2010).

Many researchers around the world have focused to study different aspects of heavy metal biosorption processes. In this regard, Ho et al. (2002) investigated removing heavy metal ions, such as Zn(II), Cu(II) and Pb(II) from aqueous solutions using tree fern. The temperature of the solution and the size of the particles were considered as the variables. The experimental results were fitted to the Langmuir, Freundlich and Redlich-Peterson isotherms to obtain the characteristic parameters of each model. Kacar et al. (2002) compared biosorptive capacities of alginate and immobilized live and heat inactivated *Phanerochaete chrysosporium* for the removal of Hg(II) and Cd(II) ions from aqueous solution. The effects of initial metal concentration, the contact time, temperature, and the pH of the medium were studied on the metal removal process. Joo et al. (2010) also compared the sorption capacities of two bacterial strains of *Pseudomonas aeruginosa* and *Bacillus cereus* for Zn (II) removal from aqueous solution. They assessed the effects of solution pH, metal ion concentrations, and the contact time between the biosorbent and the solution followed by studying the kinetic and equilibrium isotherms. In other literature, the common equilibrium isotherms were studied in order to calculate the maximum cadmium sorption capacities of dried and live biomass of *Bacillus cereus*. In addition, the biosorption characteristics were investigated as a function of initial pH, contact time, and initial cadmium concentration (Huang et al., 2013).

In the present study, the mercury biosorption process by dried indigenous bacterial strains of *Vibrio* and *Oceanimonas*, which were previously isolated by the present researchers from the contaminated sediments of Bushehr coast, is studied. Some experiments are performed in order to achieve the optimum conditions including the contact time and the initial pH of the solution. In addition, the kinetic and equilibrium parameters of the bio

sorbents are calculated by using the pseudo-first and pseudo-second order kinetic models as well as the Langmuir and Freundlich equilibrium isotherms, respectively. Finally, the most efficient biosorbent for use in mercury biosorption operations in aqueous solutions is introduced.

2 MATERIALS AND METHODS

2.1 Chemicals

All chemicals used throughout this study were of analytical grade and purchased from Merck Company. Solutions were prepared by double-distilled water. All glassware was soaked in 10% nitric acid and rinsed several times with distilled water prior to the experiments to avoid the metal contamination. The pH of the solutions was adjusted using 1 M NaOH or 1 M HCl.

2.2 Preparation of biosorbent

In previous study, mercury-resistant strains were isolated from Bushehr (Iran) coastal sediments and maintained on Tryptic Soy Agar (TSA) plates at 4 °C (Jafari et al., 2013). Two of them, *Vibrio parahaemolyticus* PG02 and *Oceanimonas baumannii* PG03 (Gen Bank accession number KC990033 and KF017584 respectively), were chosen for biosorption experiments in the form of dried biomass. They were cultured individually into a 500 ml Erlenmeyer flask containing 200 ml Tryptic Soy Broth (TSB) medium and 2.5% NaCl. The seed culture was placed in a conventional shaker incubator for 8 hr at 160 rpm and 35 °C. Initial pH measured was7.2. It was then transferred to a 10 L bioreactor (Electrolab, ferMac 360) containing four liters of TSB culture medium (5% inoculation) followed by stirring at 160 rpm and constant temperature of 35 °C. The pH was kept constant at 7.0 within the incubation period. The cells were then harvested by centrifugation (4000 rpm for 30 min at room temperature) after 48 hr of incubation during the stationary phase of growth. The precipitated biomass was then rinsed twice with double distilled water and dried in a conventional oven at 60 °C for 10 hr (Wang et al., 2010).

2.3 Batch biosorption experiments

The batch experiments were conducted in 250 ml Erlenmeyer flasks containing 100 ml Hg^{2+} solution. 0.1 g biomass was considered to be added to 100 ml metal solutions with different mercury concentrations (10, 40, and 100 mg/l). The initial pH of the solutions was adjusted to 6 and placed in a shaker incubator under 160 rpm and 35 °C. Sampling was done in specific time intervals up to 120 min of contact. The effect of initial pH of the solution was studied with 10 mg/l Hg^{2+} solution under different initial pH (in the range of 3 to 7). These experiments were also conducted under 160 rpm and 35 °C; however, sampling was done after 60 min of contact. A series of control runs including the metal solution without the biosorbent were conducted simultaneously with the main runs under the same conditions. All of the samples were centrifuged (5000 rpm for 30 min) immediately after the sampling followed by dilution in sufficient amount of double-distilled water in order to analyze the residual mercury concentration in supernatant with flameless Atomic Absorption Spectrophotometer (PG instruments, AA500, England). All set of adsorption experiments performed in duplicate and confidence intervals of 95% were calculated for each set of the samples. The biomass sorption capacity, $q(\mathrm{mg/g})$, as well as removal percentage ($\%R$) were calculated using Equations (1) and (2), respectively as follows:

$$q = \frac{(C_i - C_f).V}{m} \quad (1)$$

$$\%R = \frac{(C_i - C_f)}{C_i} \times 100 \quad (2)$$

Where C_i and C_f are the initial and residual mercury concentrations (mg/l) respectively, V is the solution volume (l) and m is the dry weight of the biomass (g).

2.4 Kinetic studies and equilibrium isotherms

The kinetic of adsorption provides the rate of sorption of metal ions onto the surface of the biosorbent (El-Sikaily et al., 2007; Esmaeili et al., 2012). There are two kinetic models namely pseudo-first order and pseudo-second order, which are more common in literature. In the present study, the mentioned models were evaluated for both of the *Vibrio* and *Oceanimonas* separately under three different mercury concentrations of 10, 40 and 100 mg/l. The experimental data were fitted by linear form of the models. They are expressed as Equations (3) and (4), respectively (Bayramoğlu and Arıca, 2008).

$$log(q_e - q_t) = logq_e - \frac{k_1}{2.303}t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{1}{q_e}t \quad (4)$$

Where $\boldsymbol{q_t}$ and $\boldsymbol{q_e}$ are the amounts of Hg^{2+} adsorbed at time $\boldsymbol{t}$ (min) and equilibrium (mg/g), respectively, and $\boldsymbol{k_1}$ is the rate constant of pseudo-first order adsorption process (1/min). The values of $\boldsymbol{k_1}$, and $\boldsymbol{q_e}$ are determined from the slope and intercept of the plot of $\boldsymbol{log(q_e - q_t)}$ against $\boldsymbol{t}$ respectively. $\boldsymbol{k_2}$ is the equilibrium rate constant of pseudo-second order biosorption (g/mg.min). Values of $\boldsymbol{k_2}$ and $\boldsymbol{q_e}$ are calculated from the plot of $\boldsymbol{t/q_t}$ against $\boldsymbol{t}$. The term $\boldsymbol{k_2 {q_e}^2}$ in equation 4, is known as the initial rate of biosorption, $\boldsymbol{h}$ (mg/g.min).

The equilibrium isotherm study is of particular importance because it represents the interactions between the biosorbents and adsorbed metal ions and also is very useful to compare the efficiency and sorption capacity of several biosorbents (El-Sikaily et al., 2007). These equilibrium experiments were conducted under a vast range of mercury concentrations (10 to 350 mg/l) by keeping constant the pH of the solution during the experiment at optimum value. Two known models of Langmuir (monolayer sorption on a homogeneous surface) and Freundlich (heterogeneous distribution of active sites) were evaluated to describe the equilibrium sorption data. The linear form of the Langmuir model is given by Equation (5) as follows (Ho et al., 2002):

$$\frac{C_e}{q_e} = \frac{1}{q_{max} b} + \frac{C_e}{q_{max}} \quad (5)$$

Where C_e is the equilibrium concentration (mg/l), q_{max} is the maximum metal uptake (mg/g) to form a complete monolayer on the surface and b is the Langmuir equilibrium constant (l/mg) that represents the affinity between the sorbent and sorbate. High b values are reflected in the steep initial slope of a sorption isotherm (Gialamouidis et al., 2010). The q_{max} and b can be determined by plotting C_e/q_e versus C_e. An efficient biosorbent can be judged according to high values of q_{max} and b (Gialamouidis et al., 2010).

The main characteristics of Langmuir isotherm is expressed by separation factor, R_L, as was given in Equation (6).

$$R_L = \frac{1}{1 + bC_i} \quad (6)$$

Where C_i and b are initial metal concentration and Langmuir constant, respectively. The value of $R_L > 1$ shows an unfavorable sorption, $R_L = 1$ a linear sorption, $0 < R_L < 1$ a favorable sorption and $R_L = 0$ indicates an irreversible sorption (Huang et al., 2013; Ho et al., 2002).

The linear form of the Freundlich model is

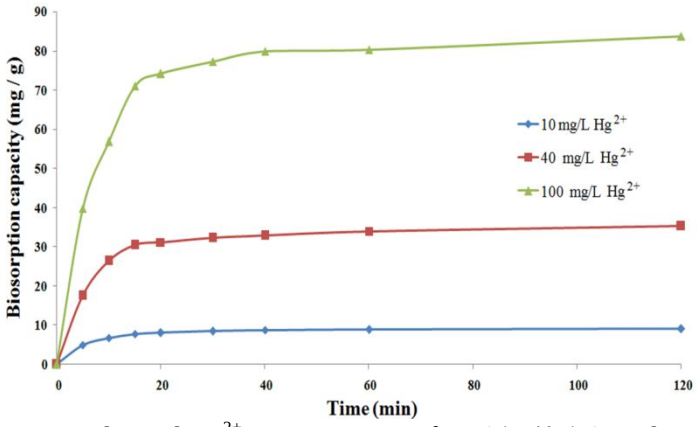

Fig. 1. Effect of contact time and initial Hg^{2+} concentrations of 10 (♦), 40 (■), and 100 (▲) mg/l on mercury adsorption capacity by *Vibrio* biomass. 160 rpm, 1 g/l biosorbent, initial pH of the medium 6, temperature 35 °C.

given as Equation (7).

$$logq_e = logk_F + \frac{1}{n} logC_e \quad (7)$$

Where k_F (mg/g) and n are the Freundlich constant and Freundlich exponent, respectively. The k_F value is an indicator of the biosorption capacity and $1/n$ represents the surface heterogeneity and are calculated from the intercept and slope of a plot of $logq_e$ versus $logC_e$, respectively (Li et al., 2010).

3 RESULT AND DISCUSSION

3.1 Effect of contact time and initial Hg^{2+} concentration on biosorption capacities

Figs 1 and 2 show the mercury biosorption by *Vibrio* and *Oceanimonas* biosorbents, respectively during 120 min contact with 10, 40 and 100 mg/l Hg^{2+} solutions at 35 °C and initial pH of 6. The biomass concentration of 1 g/l was considered as the optimum value. Increasing its dosage increased the removal percentage while decreased the sorption capacity (Unpublished date). As can been seen in Figs 1 and 2, around 50% of mercury adsorption occurred rapidly during the first 10 min of contact under different initial metal concentrations. This rapid mercury adsorption during this time was due to the high initial driving force which was established between the vacant sites on the surface of the biosorbents and high initial metal concentration in the solution. The increase in the biosorption capacities by increasing the initial metal concentration also refers to the increasing initial driving force. Although the mercury biosorption significantly increased up to thenext 10 min of contact, its rate decreased gradually up to 60 min of contact. No change was observed in mercury concentration in the solution after this time which is known as the equilibrium time. So, the equilibrium time of 60 min was considered for the following experiments. Other literature also achieved the equilibrium time of 60 min for biosorption of Hg^{2+} by dried *Bacillus* and *Lentinus edodes* (Green-Ruiz, 2006; Bayramoğlu and Arıca, 2008). The final depletion in the rate of biosorption after the initial 20 min of contact was due to the occupation of vacant sites and increasing the repulsive forces between Hg^{2+} ions on the surface of the biosorbent (Ertugay and Bayhan, 2010; Joo et al., 2010; Tunali Akar et al., 2012). *Vibrio* cells adsorbed 9.09, 35.32 and 83.79 mg Hg^{2+}/g dried biomass at initial Hg^{2+} concentrations of 10, 40 and 100 mg/l respectively after 120 min of contact (Fig. 1). The corresponding values for the other biosorbent, *Oceanimonas*, were achieved 8.08, 24.88, and 43.2 mg/g dried biomass (Fig. 2).

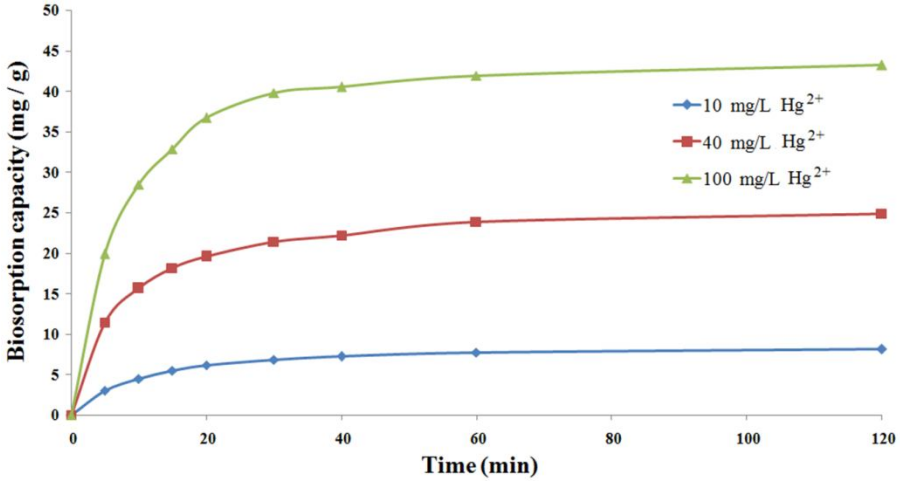

Fig. 2. Effect of contact time and initial Hg^{2+} concentrations of 10 (♦), 40 (■), and 100 (▲) mg/l on mercury adsorption capacity by *Oceanimonas* biomass. 160 rpm, 1 g/l biosorbent, initial pH of the medium 6, temperature 35 °C.

This suggests a better mercury adsorption capacity for *Vibrio* than the *Oceanimonas* biomass.

The removal percentages reduced by increasing the initial metal concentration. By increasing the initial metal concentration from 10 to 100 mg/l, it decreased from 91 to 84% and 80 to 43% for *Vibrio* and *Oceanimonas* biosorbents, respectively. The same trend of decrease in removal percentage by increasing initial mercury concentration was observed by Green-Ruiz (2006). In addition, a slight depletion in mercury concentration was observed in control runs (below 1%), which contained only the metal solution, during 120 min of contact time. It means that one percent of initial mercury concentration was not adsorbed by the biosorbents. It was considered negligible and can be due to the adsorptive effect of surface of the glassware. Stas' et al. (2004) previously proved that heavy metal ions could be adsorbed by different rates on the surface of glassware depending on the type of glass used. Sinha and Khare (2012) also observed almost 13% reduction in mercury concentration during 144 hr contact between mercury solution, without bacteria, and glass container.

3.2 Effect of initial pH on biosorption capacities

The pH of the medium is one of the most important parameters which significantly affects the biosorption process (Ertugay and Bayhan, 2010). In general, the influence of pH on the biosorption process is closely related to the ionic states of functional groups on the cell wall as well as to the metal speciation in solution (Lacher and Smith, 2002; Herrero et al., 2005). In order to study this effect, the initial pH of the medium was adjusted in the range of 3 to 7 under 10 mg/l mercury concentration and 35 °C. Fig. 3 shows the results of changes in initial pH of the solution on the sorption capacities for both of the studied biosorbents. It clearly indicates that increasing the initial pH of the solution significantly increases the metal sorption capacity.

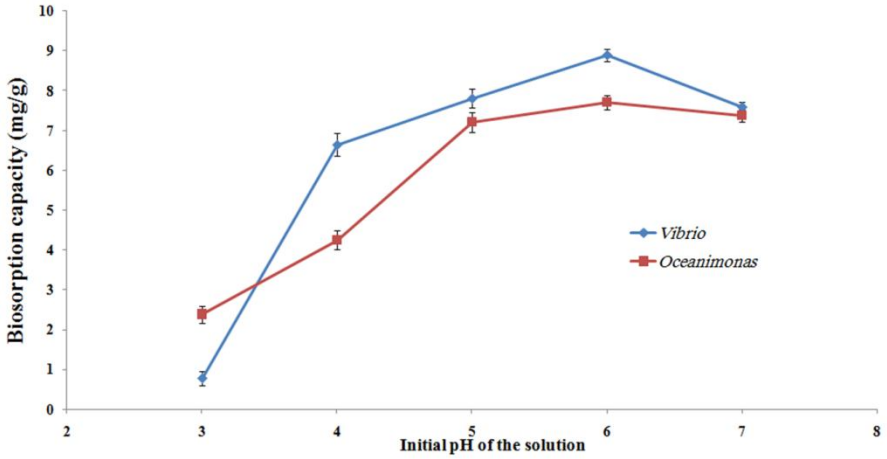

Fig. 3. Effect of initial pH of the medium on mercury adsorption capacity by *Vibrio* (♦) and *Oceanimonas* (■) biomass.160 rpm, 1 g/l biosorbent, 10 mg/l Hg^{2+}, temperature 35°C.

It is presumably due to the high concentration of H^+ ions in the solution at low pH values. This makes a severe competition between H^+ and Hg^{2+} ions for adsorption on the surface of the biosorbents. This effect is reduced by increasing the pH of the medium (Khoramzadeh et al., 2012). Probably, the specific surface ligands which contributed in the sorption of Hg^{+2} ions are destroyed under acidic medium, as Lacher and Smith (2002) also proposed. However, increasing the pH more than 6 leads to a decrease in sorption capacities for both of the biosorbents (Fig. 3). It is possible that the formation of metal hydroxides, which is negatively charged, reduced the sorption capacities of metal ions onto the surface of the cells (Kacar et al., 2002; Green-Ruiz, 2006; Joo et al., 2010). Indeed, the concentration of OH^- ions in the medium increases at pH values higher than optimum which makes a strong complex with metal ions as the following equation:

$$M^{2+} \xrightarrow{(OH)^-} MOH^+ \xrightarrow{(OH)^-} M(OH)_2 \xrightarrow{(OH)^-} M(OH)_3{}^- \xrightarrow{(OH)^-} M(OH)_4{}^{2-}$$

On the other hand, as described above, the metal speciation in the solution severely affects the metal adsorption process. As Herrero et al. (2005) showed, the dominant mercury species in the solution at pH values less than 6 is soluble Hg^{2+} ions which are easily adsorbed by the biosorbents while the dominant species at higher pH values are hydroxide complexes, which are less willing to be attracted by the biosorbent. The control runs, including only the metal solution, also demonstrated a reduction in mercury concentrations at high pH values while this was not observed at lower pH values. This can be due to the complex formation which appeared as turbidity or haze in the solution. Therefore, further experiments were performed under optimum pH value of 6.

The optimum value for pH is based on the type of metal ions and biosorbent. Other literature also found the same peak in the graphs for metal biosorption capacities versus different initial pH values (Kacar et al., 2002; Ertugay and Bayhan, 2010). In the case of mercury, several literature achieved the same optimum value for pH, 6 (Bayramoğlu and Arıca, 2008; Cain et al., 2008; Plaza et al., 2011). However, some literature achieved a value between 4 to 6 (Kacar et al., 2002; Green-Ruiz, 2006; Khoramzadeh et al., 2012; Sinha et al., 2012).

3.3 Kinetic studies

Two common kinetic models of pseudo-

first and pseudo-second order were considered to study mercury biosorption by *Vibrio* and *Oceanimonas* biomass under three different mercury concentrations of 10, 40 and 100 mg/l. The correlation coefficient value (R^2), which is obtained by data linearization, determines the predominant model. Table 1 has listed the obtained kinetic parameters along with theR^2 values at different metal concentrations. As previously mentioned, sampling was done after 60 min of contact.

As can be seen from Table 1, the calculated R^2 values for the pseudo-second order model are more satisfactory than the pseudo-first order model for both of the biosorbents. They are so close to 1. Also, the predicted values of mercury biosorption capacity for pseudo-second order model, $q_{e,model}$, are closer to experimental ones, $q_{e,exp}$, while this is not valid for the pseudo-first order model capacity values. As it has been discussed by Sinha et al. (2012), if the obtained value for $q_{e,model}$is not compatible with $q_{e,exp}$, even if the R^2 value be so close to 1, the considered kinetic model is not appropriate for the description of the experimental data. So, the proper model in this study is the pseudo-second order model.

Gupta and Rastogi (2008) investigated the kinetic behavior of biosorption of cadmium ions onto *Oedogonium*. They found that the pseudo-second-order model best described the biosorption process. Many other researchers found similar findings in their works. For example, Cruz et al. (2004) for cadmium biosorption onto *Sargassum*, Ofomaja and Ho (2007) for cadmium onto coconut copra meal, Ofomaja (2010) for Lead onto mansonia wood sawdust, Joo et al. (2010) for Zn^{2+} by *Pseudomonas aeruginosa* and *Bacillus cereus*, Li et al. (2010) for Zn^{2+}onto live and dead cells of *Streptomyces ciscaucasicus.*, Gialamouidis et al. (2010) for Mn^{2+} onto *Pseudomonas* sp and *Staphylococcus xylosus.*

Good fitting of the experimental data by the pseudo-second order model for *Vibrio* and *Oceanimonas* biosorbents is shown in Figs 4 and 5 during 60 min of contact, respectively. Lesmana et al. (2009) have cited that if the experimental data follow the pseudo-second order kinetic model, the rate of limiting step in metal biosorption process is chemisorption. So, it can be concluded that the predominant mercury biosorption mechanism in this study by *Vibrio* and *Oceanimonas* can be chemisorption e.g. ion-exchange or complex formation. As it is clear in Table 1, the rate constants of pseudo-second order model, k_2, decreased by increasing initial Hg^{2+} concentration. However, the initial adsorption rate, h, increased. It means that the increase in initial metal concentration leads to increasing the initial driving force where more ions take

Table 1
The pseudo-first order and pseudo-second order kinetic parameters for Hg^{2+} biosorption by *Vibrio* and *Oceanimonas* biosorbents at pH value of 6.

C_i(mg/l)	Biosorbent	$q_{e,exp}$ (mg/g)	pseudo-first order			pseudo-second order			
			k_1 (1/min)	$q_{e,model}$ (mg/g)	R^2	k_2 (g/mg.min)	$q_{e,model}$ (mg/g)	h (mg/g.min)	R^2
10	*Vibrio*	9.09	0.061	4.84	0.917	0.027	9.55	2.41	0.999
40		35.32	0.049	17.28	0.834	0.007	36.28	9.28	0.998
100		83.79	0.053	44	0.839	0.002	87.99	18.79	0.997
10	*Oceanimonas*	8.08	0.049	6.22	0.978	0.011	8.98	0.92	0.999
40		24.88	0.048	16.93	0.959	0.006	26.37	3.83	0.999
100		43.20	0.057	27.65	0.938	0.003	46.59	7.64	0.999

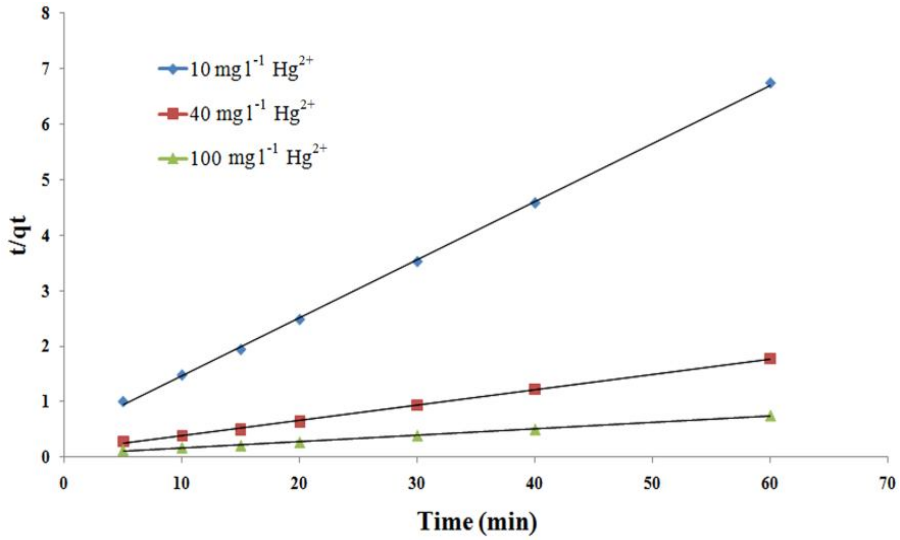

Fig. 4. The pseudo-second order kinetic model for Hg^{2+} biosorption by *Vibrio* at mercury concentrations of 10 (♦), 40 (■), and 100 (▲) mg/l. 160 rpm, 1 g/l bio sorbent, pH of 6, temperature 35 °C.

rush on the surface of the biosorbents at the same time period. But the possibility of collision of metal ions will be greater at high metal concentrations which reduces the rate of ion diffusion toward the surface of the biosorbent (Kumar and Kirthika, 2009). On the other hand, as previously discussed, the repulsive force between metal ions on the surface of the biosorbent is more at higher metal concentrations which reduces the rate of metal biosorption on the surface of the cells. Other literature have also reported the same findings (El-Sikaily et al., 2007; Kumar and Kirthika, 2009; Ofomaja, 2010).

3.4 Equilibrium isotherms

The equilibrium isotherms are applicable for the calculation of the maximum adsorption capacity of biosorbents, the biosorbent affinity to specific metal ions as well as comparing the efficiency of several biosorbents.

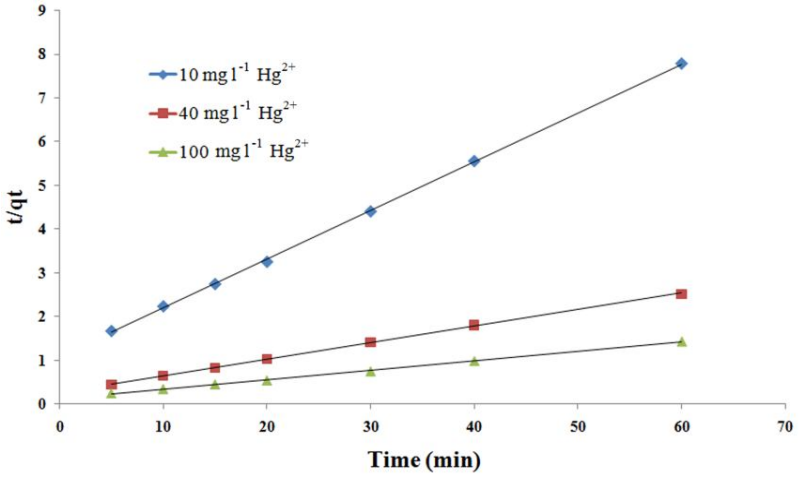

Fig. 5. The pseudo-second order kinetic model for Hg^{2+}biosorption by *Oceanimonas* at mercury concentrations of 10 (♦), 40 (■), and 100 (▲)mg/l. 160 rpm, 1 g/l bio sorbent, pH of 6, temperature 35 °C.

Table 2
The Langmuir and Freundlich equilibrium parameters for Hg^{2+} biosorption by *Vibrio* and *Oceanimonas.*

Biosorbent	Langmuir model				Freundlich model		
	q_{max} (mg/g)	b (l/mg)	R^2	R_{L350} [a]	k_F (mg/g) (l/mg)$^{1/n}$	n	R^2
Vibrio	193	0.054	0.997	0.05	12.86	1.78	0.949
Oceanimonas	113	0.015	0.953	0.15	5.07	1.87	0.998

[a] R_{L350} is the minimum value of R_L at the maximum mercury concentration.

For this purpose, the Langmuir and Freundlich isotherm models were linearized according to equations 5 and 7 to describe the experimental equilibrium biosorption of Hg^{2+} by *Vibrio* and *Oceanimonas* biomass. The temperature and pH of the medium were controlled constant at 35 °C and 6 respectively during these set of experiments. The pH adjustment seems to be necessary during these experiments. Because in this case, the pH of the medium decreased by itself during the metal adsorption experiment. It was presumably due to the ion-exchange phenomenon which led to release of H^+ ions in the medium. This was also proved by Ho (2005). Table 2 shows the obtained equilibrium parameters which were evaluated in the range of 10 to 350 mg/l mercury concentration. The R^2 values show the power of corresponding model for describing the experimental data.

As can be seen in Table 2 and Figs 6 and 7, both of the models described the experimental data with a reasonable precision for both of the biosorbents. The minimumR^2 value was achieved 0.949. However the mercury biosorption by *Vibrio* was better described by the Langmuir model (R^2= 0.997) than the Freundlich. This shows a homogenous and monolayer adsorption of Hg^{2+} ions onto the surface of the biosorbents. However, the mercury biosorption by *Oceanimonas* cells was better described by the other model, Freundlich (R^2= 0.998), which suggests a heterogeneous biosorption (Table 2). The predominant isotherm model was also determined as Langmuir for heavy metal biosorption by activated carbon derived from fertilizer waste, *Oedogonium*, *Sargassum*, alginate and immobilized live and heat inactivated *Phanerochaete chrysosporium*, dead cells of *Streptomyces ciscaucasicus*, *Pseudomonas* and *Blakeslea trispora* strains (Mohan et al., 2001; Kacar et al., 2002; Cruzet al., 2004; Gupta and Rastogi, 2008; Li et al., 2010; Gialamouidis et al., 2010). It seems that this isotherm model is more convenient in metal biosorption process.

According to the Langmuir model, the predicted values achieved for maximum biosorption capacities of *Vibrio* and *Oceanimonas* cells, q_{max}, were 193 and 113 mg Hg^{2+}/g dried biomass respectively under the defined environmental conditions. This suggests the *Vibrio* biomass as a more efficient biosorbent than the *Oceanimonas* for Hg^{2+} removal from aqueous solutions.

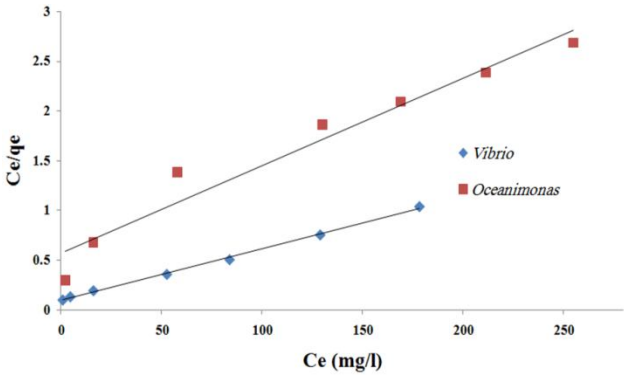

Fig. 6. The Langmuir isotherm model for Hg^{2+}biosorption by *Vibrio* (♦) and *Oceanimonas* (■) biosorbents. 60 min contact with mercury solution at concentrations of 10 to 350 mg/l, under constant temperature of 35 °C and pH of 6.

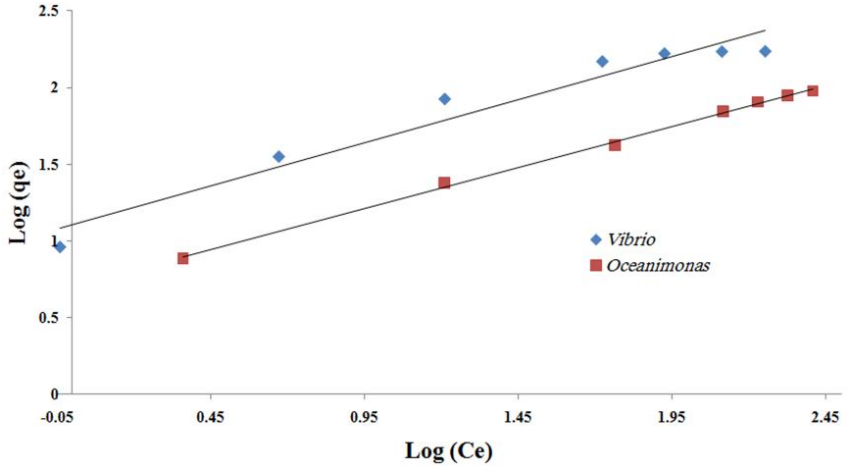

Fig. 7. The Freundlich isotherm model for Hg^{2+}biosorption by *Vibrio* (♦)and *Oceanimonas* (■) bio sorbents. 60 min contact with mercury solution at concentrations of 10 to 350 mg/l, under constant temperature of 35 °C and pH of 6.

The parameter n in the Freundlich model should give the value between 1 and 10. A bigger value shows a stronger interaction between metal ions and ligands on the surface of the biosorbents (Li et al., 2010). The value of n=1.87 was achieved for biosorption of Hg^{2+} by *Oceanimonas* (Table 2). A list of several types of biosorbents, which have been used for Hg^{2+} biosorption from aqueous solutions, is presented in Table 3 in order to compare their equilibrium isotherm parameters. According to this Table, the obtained value of n for *Oceanimonas* is greater than the others. This indicates that there is a stronger interaction between metal ions and ligands on the surface of the biosorbents. The Freundlich biosorption capacity, k_F, was given the third place for this strain among the other biosorbents (Table 3).

Table 3
The comparison of Langmuir and Freundlich parameters for Hg^{2+} biosorption by several biosorbents.

biosorbent	Langmuir parameters		Freundlich parameters		Reference
	q_{max} (mg/g)	b (l/mg)	k_F (mg/g) (l/mg)$^{1/n}$	n	
Vibrio	193	0.054	-	-	This study
Oceanimonas	-	-	5.07	1.87	This study
walnut shell activated carbon	151.5	0.009	-	-	Zabihi et al., 2010
Native *Lentinus edodes*	358.1	0.077	-	-	Bayramoğlu and Arıca, 2008
Inactive *Lentinus edodes*	419.1	0.145	-	-	Bayramoğlu and Arıca, 2008
Sugarcane Bagasse	-	-	5.77	0.55	Khoramzadeh et al., 2012
sewage sludge activated carbons	-	-	10.1	1.04	Zhang et al., 2005
Ulva lactuca	149.25	0.788	-	-	Zeroual et al., 2003
Sargassum glaucescens	-	-	0.77	1.10	Esmaeili et al., 2012
Bacillus sp.	-	-	3.15	1.51	Green-Ruiz, 2006
Bacillus cereus	104.1	0.171	-	-	Sinha et al., 2012

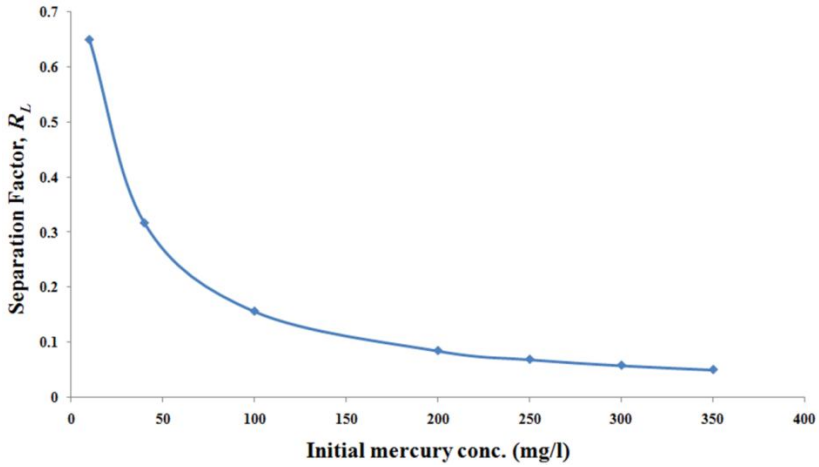

Fig. 8. Change in R_L parameter by different initial Hg^{2+}concentrations for *Vibrio* biosorbent.

The Langmuir constant, b, fordried *Vibrio* cells is less than the rest of the biosorbents except the walnut shell activated carbon. This indicates a lower affinity for the biosorbent to mercury ions. So, it is expected that its initial slope of the isotherm be less than the other biosorbents in Table 3 (Gialamouidis et al., 2010). Its maximum adsorption capacity is a high value and is given the third place in Table 3 that suggests a potent biosorbent for mercury removal from aqueous solutions.

The R_L value is changed by initial metal concentration according to Equation 6. The obtained values for this parameter were in the range of 0.05 to 0.6 for *Vibrio* biosorbent (which was better described by the Langmuir isotherm) and this implies a favorable biosorption process (Fig. 8). Other researchers as Ho et al. (2002) and Tunali Akar et al. (2012) observed the same trend of Fig. 8. So, the dried biomass of *Vibrio* shows a good potential for mercury removal from aqueous solutions especially at concentrations below 100 mg/l (with more than 80% efficiency). Since it is an indigenous strain and easy to culture, it can be considered as an available and valuable biosorbent for mercury biosorption from aqueous solutions.

4 CONCLUSION

In this study, the mercury biosorption capacity for two indigenous strains of *Vibrio* and *Oceanimonas* in the form of dried biomass was evaluated and compared. A series of batch experiments by both biosorbents show that about 50% of initial metal was rapidly adsorbed during the first 10 min of contact followed by gradual decrease to reach the equilibrium after about 60 min of contact and no mercury removal occurred after this time. Increasing initial metal concentration from10 to 100 mg/l increased the metal biosorption but did not affect the equilibrium time. However, the removal percentage decreased from 91 to 84% and 80 to 43% for *Vibrio* and *Oceanimonas* biosorbents, respectively. Increasing the initial pH of the solution up to 6 increased the mercury biosorption while the higher values had a reverse impact. The maximum mercury biosorption by these biosorbents occurred at pH value of 6. Kinetic studies under different Hg^{2+} concentrations revealed that the pseudo-second order model was more successful to describe the experimental biosorption data than the pseudo-first order model for both the biosorbents. This can imply the presence of a chemisorption mechanism on the surface of the biosorbents. Evaluation of two common

isotherm models, Langmuir and Freundlich, shows that metal biosorption by *Vibrio* biomass was better described by the Langmuir model that implies a monolayer sorption on a homogeneous surface. While the mercury biosorption by *Oceanimonas* biomass was a heterogeneous biosorption and follows the Freundlich models. The maximum mercury biosorption capacities according to the Langmuir model were achieved 193 and 113 mg Hg^{2+}/g dried biomass for the *Vibrio* and *Oceanimonas*, respectively. So, dried biomass of *Vibrio* can be used as a good biosorbent for mercury removal from aqueous solutions due to its availability, indigenous strain, easy to culture, and high efficiency especially at low mercury concentrations.

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