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Equilibrium studies of the sorption of Hg(II) ions onto chitosan

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Abstract

Chitosan is a biopolymer found in the body of the shellfish, crustaceans and some fungi. The free amino groups of this biopolymer show different properties such as anti-microbial, anti-acid and chelating of metal ions. Chitosan has been used as an adsorbent for the removal of the metal ions from industrial effluents. In this paper, the sorption of mercuric ions from solution onto chitosan particles with sizes of 0.177, 0.5 and 1.19 mm at three initial pH 3.00, 4.50, 6.00 ± 0.1 has been investigated. The experimental data were analyzed using the Langmuir, Freundlich and Redlich–Peterson equations. Error function and correlation coefficients were determined for each isotherm analysis. The results showed that increasing of pH increased the extent of Hg(II) ions uptake and decreasing of adsorbent particle sizes increased the amount of mercury removals. The study of equilibrium isotherm shows that the best model for analysis of experimental data is Langmuir model with correlation coefficient higher than 0.982. Maximum Hg(II) ions uptake with chitosan in our experiments (from Langmuir equation) is 1127.1 (mg Hg^{2+}/g chitosan).

Keywords: Adsorption; Chitosan; Heavy metals; Mercury ions

1. Introduction

Waste waters containing heavy metals pollutants come from different industrial activities such as mining, power plants, plating facilities and electrical equipment manufacturing. All heavy metals are toxic and non-biodegradable and should be separated from waste waters.

There are several ways for separation of heavy metals from waste water such as chemical separation, filtration, membrane separation, electro chemical treatment, ion exchange and adsorption. All these methods, with the exception of adsorption are costly, have low output and are incapable of removing trace level of heavy metal ions from waste water. Adsorbents can be used for water and waste water treatment and indeed they are widely used due to their higher output and lower costs. Among current adsorbents, activated carbon is used in different industries, but it is not a selective adsorbent.

Recently, a number of studies were carried out on low cost adsorbents from natural resources. The use of low cost adsorbents for heavy metals derived from natural resources has been reviewed by Bailey et al. [1] and Babel and Kurniawan [2]. Such a low cost adsorbent is chitosan which is a biodegradable and biocompatible polymer, produced by deacetylation of chitin. The molecular structure of chitosan is shown in Fig. 1. Chitin is a structural polysaccharide of crustaceans, insects and some fungi and is the most available biopolymer after cellulose [3,4].

Chitosan also possesses anti-microbial, anti-acid and metal-ion adsorbing properties which results in its utilization in many industrial applications [5,6]. One of the applications of chitosan and its derivatives is for separation of heavy metal ions. Adsorption of Uranyl ions [7], Ni^{2+} [8], Vanadium ions [9], Cr ions [10], Cd ions [11], Cu(II) ions [8,10,12,13,15], and heavy metals [14,16] on chitosan with different sources have been studied and also adsorption of metal ions on chitosan derivatives such as cross linked chitosan [17], polyaminated highly porous chitosan [18], chitosan beads [19,20], composite chitosan [21] and new chitosan derivatives [22–24] were investigated. These studies show that chitosan and its derivatives can be used as a adsorbent, since its amino and hydroxyl groups can act as chelating sites.

Mercury (Hg) is a highly toxic metal that is very poisonous for living organisms even in trace concentration (ppb) and therefore, before the disposal of mercury containing industrial wastes their mercury content should be eliminated. Many researches were published on removing of Hg ions by different adsorbents such as natural and industrial materials, granular activated carbon, char, pozzolana and yellow tuff [25], and mercury removal by organic cells was investigated by Green-Ruiz [26]. There are

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Nomenclature

a_L	Langmuir isotherm constant (L/mmol)
a_R	Redlich–Peterson isotherm constant (L/mmol)
b_F	Freundlich isotherm exponent constant
C_e	metal ion concentration on solution at equilibrium (mmol/L)
C_0	initial concentration of solute in solution (mmol/L)
K_F	Freundlich isotherm constant (L/g)
K_L	Langmuir isotherm constant (L/g)
K_R	Redlich–Peterson isotherm constant (L/g)
m	mass of adsorbent (g)
pH_e	pH of solution after equilibrium
q_e	metal ion concentration on adsorbent at equilibrium (mmol/g)
q_m	maximum adsorption capacity (mmol/g)
v	volume solution (L)
Greek letter	
β	Redlich–Peterson isotherm exponent constant

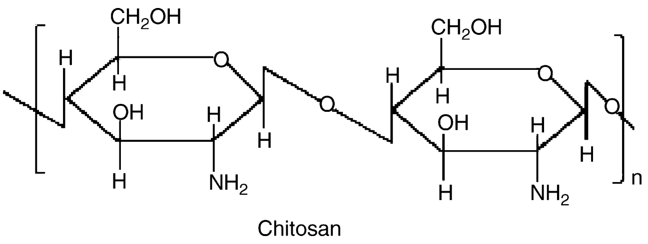

Fig. 1. Molecular structure of chitosan.

a few studies for treatment and removing of this heavy metal by chitosan [27]. In other studies maximum adsorption capacity of chitosan for Hg(II) was obtained about 815 mg/g and 123.8 mg/g chitosan, respectively [16,28]. Choong and Wolfgag have studied mercury removal by chitosan derivative, maximum removing capacity was 2.3 mmol/g at pH 7 for chitosan beads which has reacted with ethylendiamine [23]. But the effect of several parameters such as pH and particle size of adsorbent on the adsorption of Hg to chitosan system has not been considered.

In the present research, the equilibrium sorption of Hg(II) ions onto chitosan and the effect of pH and particle size of adsorbent on the adsorption rate and adsorption capacity of chitosan have been studied. The equilibrium experimental data would be analyzed by using three equilibrium isotherms including Langmuir, Freundlich and Redlich–Peterson.

2. Material and methods

2.1. Preparation of chitosan

Commercial chitosan with minimum 85% deacetylation was purchased from Sigma Co. Then it was sieved and separated into three different particle sizes, each part consists of particle sizes of 0.177, 0.5 or 1.19 mm. For removing the impurity of adsorbent, each part was separately poured in deionized water and boiled for 30 min. Then it was washed several times with deionized water and dried in a vacuum oven for 3 days at 60 °C. All dried samples were kept in desiccator [15].

2.2. BET of chitosan

The surface area (S_{BET}) of chitosan was determined from adsorption–desorption isotherm of N2 at 77 K. A Quantachrom NOVA 1000 surface area analyzer was used for measuring this parameter by applying the 3-point BET (Brunaeur–Emmet–Teller). Before measuring the isotherm, the sample was heated at 373 K for 2 h in vacuum for degassing. The pore volumes were calculated by the BJH method.

It was found that the surface area of chitosan is about 12.5 m^2/g. Pore volumes and average pore diameter of sample was 0.01 cm^3/g and 39.35 Å, respectively.

2.3. Preparation of standard solution

Mercury chloride ($HgCl_2$) with purity of 99.9% (Merk Company) deionized water were used in the preparation of solutions. Solutions with initial concentration of 0.5, 1, 2 and 3 mmol/L from $HgCl_2$ were prepared. Initial pH of solution was adjusted to 3.0, 4.5 or 6.0 ± 0.1 by NaOH solution and HCl solution (0.1 M). Also the value of pH at the end of each experiment was measured (pH_e).

2.4. Adsorption experiments

Solution with known pH was made, and then 50 mL of this solution was poured in a 250 cm^3 flask, 0.03 g of chitosan was added, and then the sealed flask was placed in a shaking incubator with speed of 300 rpm and temperature of 25 °C. After 24 h, adsorbent was separated with 0.45 μm membrane and the solution concentration was analyzed using atomic absorption spectrophotometer (model Varian CP3800). Adsorbance was measured at wave length of 253.7 nm and spectral band width of 0.5 nm. The amount of metal ion sorbed on the chitosan, q_e, was computed by the following equation:

$$q_e = \frac{v}{m}(C_0 - C_e) \qquad (1)$$

where C_e and C_0 are respectively concentrations of mercury ion in liquid after equilibrium and initial concentration of this ion in solution, whereas v and m are solution volume and mass of adsorbent, respectively.

2.5. Equilibrium isotherms

Adsorption isotherms describe how adsorbates interact with adsorbents and so are critical in optimizing the use of adsorbents. Thus, the correlation of equilibrium data by either theoretical or empirical equations is essential for practical design and operation of adsorption systems. In this study three isotherms have been investigated including, Langmuir, Frendlich and Redlish-Peterson.

2.5.1. Langmuir isotherm

The Langmuir adsorption isotherm assumes that the adsorbed layer is one molecule in thickness and that all sites are equal, resulting in equal energies and enthalpies of adsorption. The strength of the intermolecular attractive forces is believed to fall off rapidly with distance [29]. This equation for the Langmuir is as follows:

$$q_e = \frac{K_L C_e}{1 + a_L C_e} \tag{2}$$

linear form of this equation is:

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L} C_e \tag{3}$$

where a_L and K_L are the Langmuir isotherm constants. According to Langmuir equation, maximum adsorption capacity (mmol/g) is derived from the following equation:

$$q_m = \frac{K_L}{a_L} \tag{4}$$

2.5.2. Freundlich isotherm

This isotherm predicts that the Hg ion concentration on the adsorbent will increase as long as there is an increase of ion concentration in the liquid. Such an isotherm is another form of Langmuir isotherm which was stated for amorphous surfaces. The amount adsorbed is summation of the adsorption of all sites, each having bond energy. Equation of this isotherm is as follows [29]:

$$q_e = K_F C_e^{b_F} \tag{5}$$

K_F is the Freundlich constant and b_F is the Freundlich exponent. Linear form of this equation is as follows:

$$\ln\ q_e = b_F \ln\ C_e + \ln\ K_F \tag{6}$$

2.5.3. Redlich–Peterson isotherm

Such an isotherm is a combination of two previous models [29] which is defined as follows:

$$q_e = \frac{K_R C_e}{1 + a_R C_e^{\beta}} \tag{7}$$

where a_R and K_R are the constants of Redlich–Peterson and β is the exponent of equation which lies between 0 and 1. When $\beta = 1$, this equation changes to Langmuir isotherm and when $\beta = 0$, it changes to Henry equation which is defined as follows:

$$q_e = \frac{K_R C_e}{1 + a_R} \tag{8}$$

Redlich–Peterson equation can be expressed in linear form as follows:

$$\ln\ \left(K_R \frac{C_e}{q_e} - 1\right) = \ln\ a_R + \beta \ln\ C_e \tag{9}$$

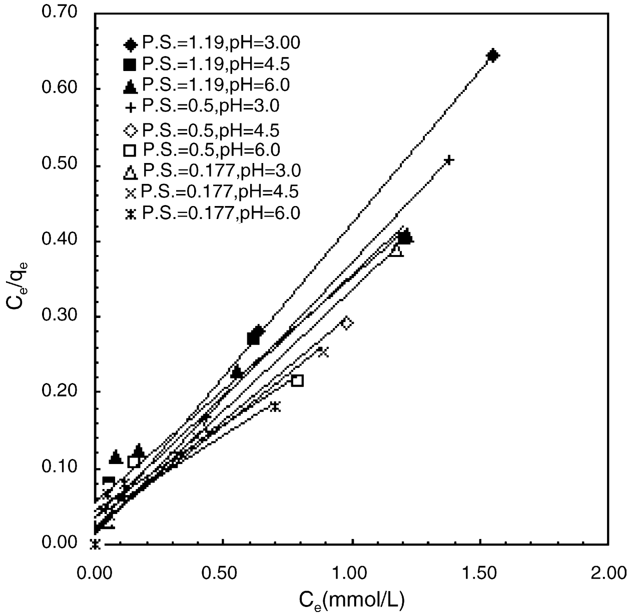

Fig. 2. Linear form of Langmuir isotherm for mercury ions/chitosan system.

3. Results and discussion

3.1. Equilibrium study

The equilibrium adsorption of Hg ion onto chitosan at three initial pH and three particle sizes was investigated. In order to optimize the design of sorption system to remove metal ions from effluents, it is important to establish the most appropriate correlation for the equilibrium curve. Three isotherm equations including Langmuir, Freundlich and Redlich–Peterson, described on the previous section, have been tested in this study.

The Langmuir and Freundlich parameters were obtained by plotting C_e/q_e versus C_e (Fig. 2) and $\ln q_e$ versus $\ln C_e$ (Fig. 3), but plotting the $\ln\{K_R(C_e/q_e) - 1\}$ versus $\ln C_e$ to obtain the

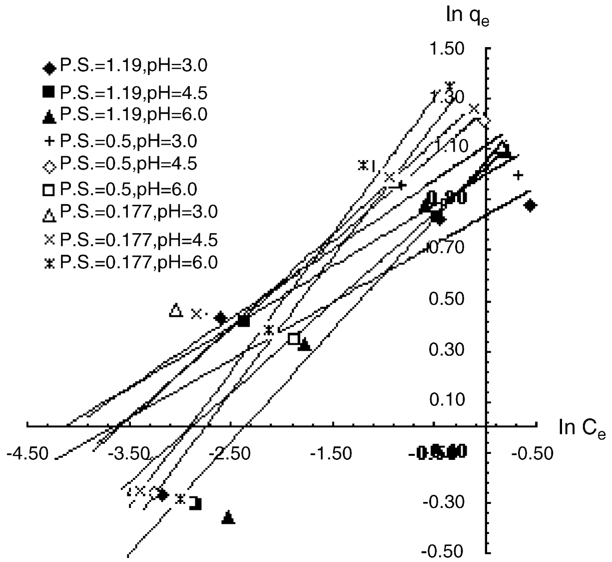

Fig. 3. Freundlich isotherm for mercury ions/chitosan adsorption system.

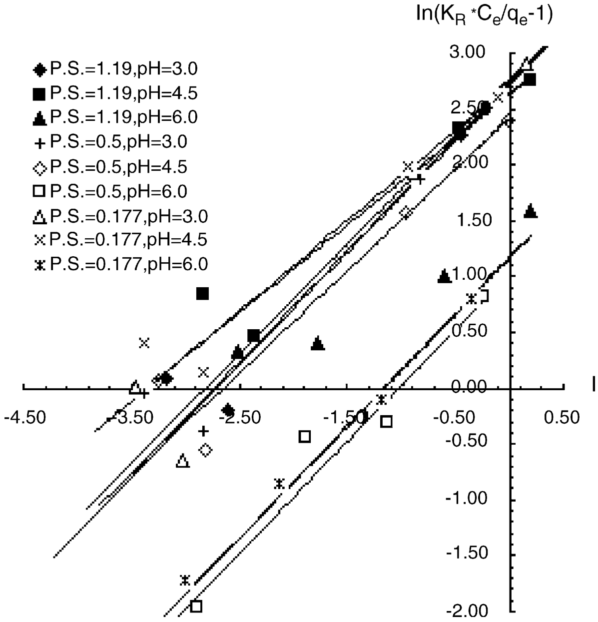

Fig. 4. Redlich–Peterson isotherm for mercury ions/chitosan adsorption system.

Redlich–Peterson constants is not possible; hence, the isotherm constants are determined by minimizing the error between the experimental data. The isotherm parameters were determined using the solver add in Microsoft Excel. The linearized form of the Redlich–Peterson isotherm is presented in Fig. 4. Tables 1–3 show the values of the parameters of three isotherms, the value of the regression coefficient R^2 and the total square of errors.

The plots in Figs. 2 and 4 demonstrate that the Langmuir and Redlich–Peterson equation provide an accurate description of the experimental data. This is confirmed by the fact that the correlation coefficients (R^2) of all experimental systems are greater than 0.982 and 0.972 for Langmuir and Redlich–Peterson, respectively, as shown in Tables 1 and 3. But Langmuir isotherm shows a better fit to adsorption data in all cases than $\beta \neq 1$ in Redlich–Peterson equation. In the other cases that β equals to 1, the Redlich–Peterson isotherm changed to Langmuir isotherm indicating that the Langmuir model is the best model for interpretation of experimental results. In all cases, the Freundlich isotherm represents the poorest fit to adsorption data among the other isotherm equations (Table 2). The fact that the Langmuir isotherm fits the experimental data very well may be due to homogenous distribution of active sites on the chitosan surface; since the Langmuir equation assumes that the surface is homogenous and all sites have equal adsorption energies [15,30]. The maximum adsorption capacity of chitosan is calculated after determination of model parameters and by use of Eq. (4) that is reported in Table 1.

Table 1
The Langmuir constants for mercury/chitosan adsorption system

	K_L (L/g)	a_L (L/mmol)	q_m (mmol/g)	ERRSQ	R^2
P.S. = 1.19 mm					
pH_0 3.0	38.02966	15.02537	2.53103	0.09135	0.990
pH_0 4.5	22.22536	7.083954	3.137423	0.199361	0.982
pH_0 6.0	12.05827	3.203808	3.763705	0.008335	0.999
P.S. = 0.5 mm					
pH_0 3.0	44.98237	15.41168	2.918719	0.094022	0.991
pH_0 4.5	34.31058	9.443129	3.63339	0.135624	0.991
pH_0 6.0	15.15137	2.776619	5.456769	0.105178	0.994
P.S. = 0.177 mm					
pH_0 3.0	48.11765	15.24196	3.15692	0.131109	0.991
pH_0 4.5	35.71216	9.542803	3.742313	0.1663	0.991
pH_0 6.0	17.76686	3.160546	5.621462	0.01004	0.999

Table 2
Freundlich isotherm constants for adsorption of mercury onto chitosan

	K_F (L/g)	b_F	ERRSQ	R^2
P.S. = 1.19 mm				
pH_0 3.0	2.3080	0.2291	0.25388	0.924
pH_0 4.5	2.7856	0.3561	0.17612	0.969
pH_0 6.0	2.8489	0.4432	0.12611	0.980
P.S. = 0.5 mm				
pH_0 3.0	2.7134	0.2414	0.41653	0.914
pH_0 4.5	3.5002	0.3464	0.24115	0.970
pH_0 6.0	4.3348	0.5327	0.28468	0.973
P.S. = 0.177 mm				
pH_0 3.0	3.0442	0.2736	0.30932	0.950
pH_0 4.5	3.7242	0.3673	0.15884	0.982
pH_0 6.0	4.8108	0.5398	0.14937	0.987

3.2. Effect of pH

One of the most important parameters in the adsorption process is initial pH of solution. Effect of pH on equilibrium adsorption of Hg ion is presented in Fig. 5. As indicated, rate of absorption at pH 6 is more than that in other cases. Because at low solution pH, the amine groups are protonated to varying degrees, reducing the number of binding sites available for mercury uptake [13]. As a result, the extent of mercury uptake is low in the presence of high concentrations of protons. Besides the pH effect on monolayer adsorption capacity (q_m) can be seen in Table 1, which shows that increasing the pH caused increasing q_m. In studies done by Chu [13], the best pH for adsorption of copper onto chitosan was 6.

Table 3
Redlich–Peterson isotherm constants for adsorption of mercury ions onto chitosan

	K_R (L/g)	β	a_R (L/mmol)	ERRSQ	R^2
P.S. = 1.19 mm					
pH_0 3.0	38.02872	1	15.02477	0.090135	0.990
pH_0 4.5	41.45797	0.78279	13.91769	0.158789	0.972
pH_0 6.0	12.05817	1	3.203775	0.008335	0.999
P.S. = 0.5 mm					
pH_0 3.0	44.98248	1	15.41174	0.088482	0.991
pH_0 4.5	40.93002	0.911235	11.20945	0.122007	0.985
pH_0 6.0	15.15138	1	2.77662	0.105178	0.994
P.S. = 0.177 mm					
pH_0 3.0	50.06292	0.981179	15.83983	0.130175	0.988
pH_0 4.5	57.39349	0.807179	15.03649	0.108347	0.979
pH_0 6.0	17.76669	1	3.160505	0.01004	0.999

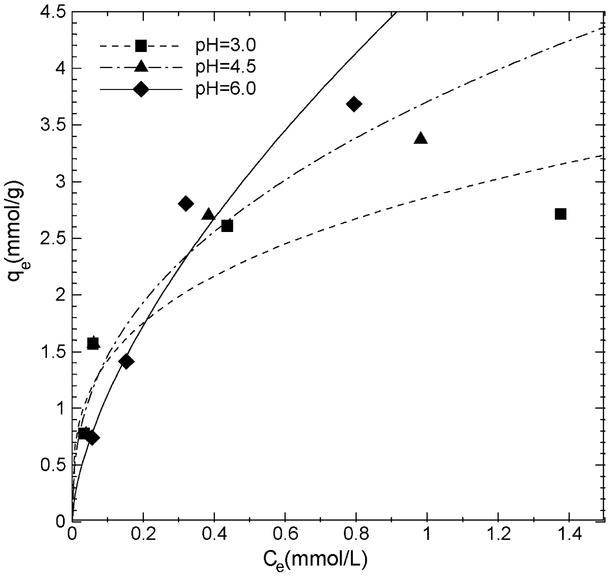

Fig. 5. Effect of initial pH on equilibrium adsorption onto chitosan (particle size = 1.19 mm).

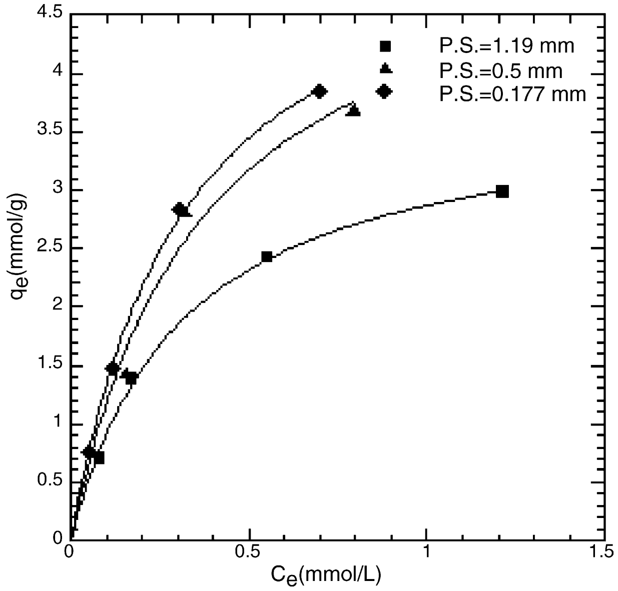

Fig. 7. Effect of particle sizes on equilibrium adsorption of mercury ions onto chitosan (initial pH 6.0).

In Fig. 6, pH_e versus C_e for particle size of 1.19 mm is plotted. The values of pH_e are different with regard to concentration of Hg ion in solution, amount of added chitosan to solution and initial pH of solution. As indicated, pH increases due to reaction of proton with chitosan which leads to a decrease in proton concentration. It is indicated that protons can compete with Hg ions to occupy the active adsorbent sites.

3.3. *Effect of particle size*

The other effective parameter is particle size of adsorbent. Maximum uptake of adsorption is a function of specific surface or external surface of adsorbent. In these series of experiments, three particle sizes with mean diameter of 0.177, 0.5 and 1.19 mm were used. Results showed that the rate of adsorption increases with decreasing particle size. In Fig. 7 effect of particle size on adsorption rate at pH 6.0 is shown. This would indicate that adsorption is limited by external surface and that intraparticle diffusion is reduced [15]. In studies performed by McKay and co-workers [15], the best particle size for adsorption on chitosan was the smallest size employed.

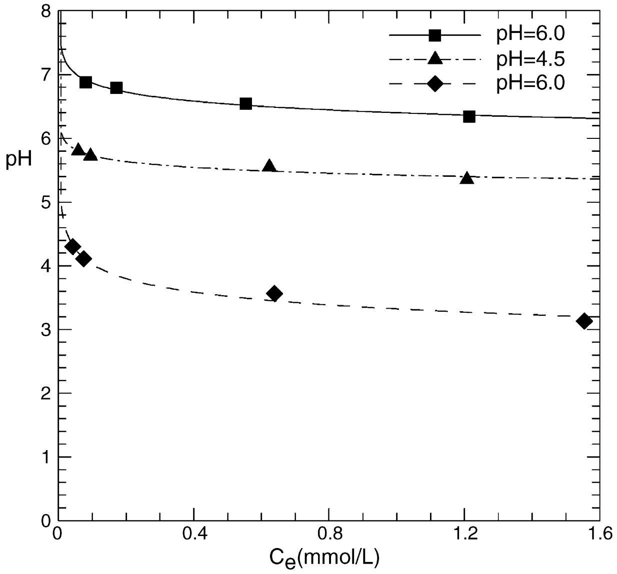

Fig. 6. Effect of equilibrium adsorption onto chitosan on pH (particle size = 1.19 mm).

3.4. *Maximum capacity of chitosan*

Maximum capacity of chitosan for adsorbing Hg has been reported in Table 1 by using Eq. (4) for all tested conditions in this research. This parameter was computed 5.62 (mmol/g) or 1127.1 (mg Hg^{2+}/g chitosan) in the best condition for chitosan/mercury system (pH 6 and particle size of 0.177 mm). Maximum capacity at equilibrium adsorption of Hg^{2+} on chitosan has previously been reported as 815 mg Hg^{2+}/g chitosan [16] and 123.8 mg Hg^{2+}/g chitosan [28].

4. Conclusions

- Langmuir model is the best model among three presented equilibrium models in this study to describe Hg^{2+}/chitosan adsorption system.
- Results show that pH 6.0 is the optimal pH for adsorption of Hg^{2+} onto chitosan.
- The best adsorbent size in this study is 0.177 mm and it can be concluded that the effective surface is the external surface of chitosan.
- Maximum capacity of chitosan for adsorbing Hg ions at the best condition in our experiments was obtained 5.62 (mmol/g) or 1127.1 (mg Hg^{2+}/g chitosan) which is comparable with the results of other published researches.

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