



Studies on efficiency of guava (*Psidium guajava*) bark as bioadsorbent for removal of Hg (II) from aqueous solutions

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ABSTRACT

Biosorption of Hg (II) was investigated in this study by using guava bark powder (GBP). In the batch system, effects of various parameters like contact time, initial concentration, pH and temperature were investigated. Removal of Hg (II) was pH dependent and was found maximum at pH 9.0. Based on this study, the thermodynamic parameters like change in standard Gibb's free energy (ΔG^0), standard enthalpy (ΔH^0) and standard entropy (ΔS^0) were evaluated. The rate kinetic study was found to follow second-order. The applicability of Freundlich adsorption isotherm model was tested. The value of regression coefficient was greater than 0.99. This indicated that the isotherm model adequately described the experimental data of the biosorption of Hg (II). Maximum adsorption of 3.364 mg g^{-1} was reached at 80 min. The results of the study showed that guava bark powder can be efficiently used as a low-cost alternative for the removal of divalent mercury from aqueous solutions.

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1. Introduction

Heavy metals are present in different types of industrial effluents, being responsible for environmental pollution. The presence of heavy metals in aquatic environment is known to cause severe damage to aquatic life, besides these metals kill microorganisms during biological treatment of water purification. Important sources of mercury are chlor-alkali industry, coal combustion and electrical batteries. Over-exposure to Hg (II) leads to nerve damage, kidney damage and brain damage reported by Rai et al. [1]. The recommended permissible limit of Hg (II) in potable water is 0.001 mg L^{-1} . Physico-chemical methods, such as precipitation, chemical oxidation or reduction, electrochemical treatment, evaporative recovery, filtration, ion-exchange and membrane technologies have been widely used to remove heavy metal ions from waste water. These processes may be ineffective or expensive, especially when the heavy metal ions are 1–100 mg dissolved heavy metal ions per liter as in the books authored by Volesky [2,3]. As studied by Kapoor and Viraraghavan [4], Eccles [5], Chen and Wang [6] biological methods such as bioaccumulation/biosorption for the removal of heavy metal ions may provide an alternate to physico-chemical methods because of their being cost effective and technically easy.

In the recent years, investigations have been carried out by Babel and Kurniawan [7], Huang and Blankenship [8], Iqbal et al., [9] and Helal [10] for the effective removal of heavy metals from waste water using low-cost, non-conventional adsorbents which are economically viable. The main focus is on the use of various industrial wastes, agricultural byproducts and biological materials as adsorbents studied by Low et al. [11], Orhan and Buyukgungar [12], Tiwari et al. [13]. Natural materials that are available in large quantities or certain waste from agricultural operations could be potential low-cost adsorbents, as they represent unused resources reported by Raji and Anirudhan [14], Muhammad et al. [15], Freeland et al. [16]. As demonstrated by Flynn et al. [17], Friedman and Waiss [18], Deshkar et al. [19] adsorption onto low-cost adsorbents, such as bark powder now offers an attractive and inexpensive option for removal of mercury. The abundant availability of bark powder makes it economically feasible. This paper deals with the equilibrium studies, which gives an idea about the capacity of the adsorbent. The equilibrium relationship between adsorbent and adsorbate is described by the adsorption isotherm which is usually the quantity adsorbed and the remaining in solution at a fixed temperature at equilibrium as discussed by Namasivayam and Yamuna [20].

2. Experimental

2.1. Adsorbate preparation

The aqueous solution of divalent mercury was prepared by dissolving known quantity of mercuric nitrate in double distilled

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Nomenclature

C_0	initial concentration of Hg (II) solution (mg L^{-1})
C_e	equilibrium concentration of Hg (II) solution (mg L^{-1})
EC	Electrical conductivity (Mho)
ΔG^0	standard Gibb's energy of adsorption (kcal mol^{-1})
ΔH^0	standard enthalpy of adsorption (kcal mol^{-1})
k	second-order rate constant ($\text{g mg}^{-1} \text{ min}$)
K_C	equilibrium constant
K_F	Freundlich multilayer adsorption capacity (mg g^{-1})
m	weight of adsorbent (g)
n	adsorption intensity
q_e	amount adsorbed at equilibrium (mg g^{-1})
q_t	amount adsorbed at time t (mg g^{-1})
R	gas constant ($\text{J K}^{-1} \text{ mol}^{-1}$)
R^2	Regression coefficient
ΔS^0	standard entropy of adsorption ($\text{cal mol}^{-1} \text{ K}^{-1}$)
t	time (min)
T	temperature (K)
V	volume (L)

water. It was further diluted to obtain standard solutions. The pH of the solution was varied using either sulphuric acid or sodium hydroxide. All the reagents used were of analytical grade.

2.2. Adsorbent preparation

Guava bark powder (GBP) used as an adsorbent was collected from Lucknow, India and washed repeatedly with deionized water to remove the water soluble impurities and other surface adhered particles. Barks were first air-dried and then dried in a pre-heated oven at 378 K for 2.5 h to get rid of the moisture and other volatile impurities. The dried bark pieces were crushed in a rotary crusher and sieved with 150 μ mesh sieve and stored in desiccators. The analysis of the raw material is given in Table 1.

2.3. Batch adsorption studies

Batch adsorption studies were conducted in a temperature-controlled shaker using 100 mL of adsorbate solution and a fixed adsorbent dosage of 1 g. The agitation speed of the shaker was fixed at 125 rpm for all batch experiments. Samples at different time intervals (10–120 min) were taken and centrifuged. The concentrations of the samples were analysed in Genesys-10 UV-vis spectrophotometer using Dithizone in carbon tetrachloride as the complexing agent at the wavelength of 490 nm as reported in APHA [21]. Isotherm studies were conducted in a series of 250 mL Erlenmeyer flasks. Each flask was filled with 100 mL Hg (NO_3)₂ solution of different initial concentrations and 1 g adsorbent was added. The solution was adjusted to pH 9.0. After equilibration the samples

Table 1
Analysis of guava bark powder

Characteristics	Value
pH	7.15
EC (Mho)	0.9012
Specific gravity	1.1812
Solubility in water (g L^{-1})	7.6
Particle size (μ mesh)	150
Moisture content (%)	3.75
Ash content (%)	9.0
Volatile matter (%)	5.8
Carbon (%)	81.45

were analysed for their Hg (II) content. Adsorption studies were carried out at different temperatures (303, 313, and 323 K) to obtain equilibrium isotherms. The initial concentrations of Hg (II) solution taken for this study were 30, 40 and 50 mg L^{-1} . The equilibrium adsorption capacity was calculated using the equation given below:

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

where q_e (mg g^{-1}) is the equilibrium adsorption capacity, C_0 and C_e are the initial and equilibrium concentration (mg L^{-1}) of Hg (II) ions in solution, V (L) is the volume and m (g) is the weight of adsorbent.

3. Results and discussion

3.1. Effect of initial concentration and time

The amount of mercury adsorbed for different initial concentrations onto GBP is shown in Fig. 1. The adsorption of Hg (II) onto GBP increased with time and attained equilibrium value at 80 min. The removal of mercury was found to be dependent on the initial concentration; the amount adsorbed was increased with increase in initial concentration. Further, the adsorption was fast in the early stages and then attained an asymptotic value for larger contact time. On changing the initial concentration from 30 to 50 mg L^{-1} , the amount of Hg (II) adsorbed increased from 1.814 to 3.268 mg g^{-1} at 303 K for a period of 80 min.

3.2. Effect of pH

The pH of the system determines the adsorption capacity due to its influence on the surface properties of GBP. Change of adsorption capacity of Hg (II) on GBP with pH is shown in Fig. 2. It was observed from Fig. 2 that adsorption capacity increased from 2.292 to 3.364 mg g^{-1} from acidic to alkaline conditions and the maximum adsorption occurred at pH 9.0 and hence it was taken as the optimal value for further adsorption studies. Thus, mercury was better removed by GBP in slightly alkaline solutions. This action is a result of the competition with H^+ ions, which can protonate the sorption sites of GBP. At low pH values, acidic protons compete with the metal, thus cause a decrease in removal. At high pH, the reaction sites are deprotonated and negatively charged, so attract the metal and the removal increases. At pH greater than 9.0 the adsorption of mercury (II) becomes slightly low which may be attributed to the formation of hydroxy species such as $[\text{Hg}(\text{OH})]^+$ or $\text{Hg}(\text{OH})_2$

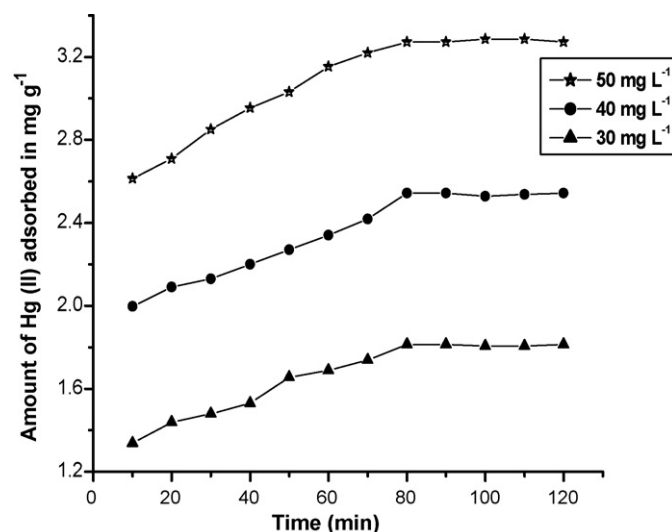


Fig. 1. Effect of initial concentration and time at $T=303$ K and pH 9.0.

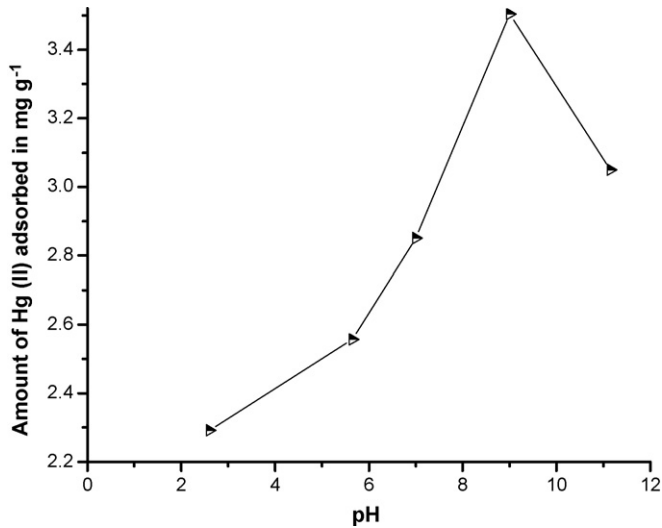


Fig. 2. Effect of pH for the concentration of 50 mg L⁻¹ at T = 303 K.

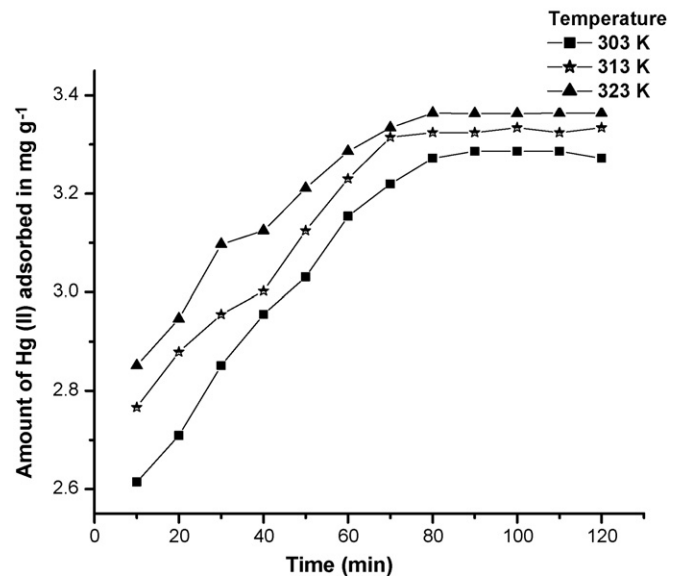


Fig. 3. Effect of temperature for the concentration of 50 mg L⁻¹ at pH 9.0.

and these may not form as strong complexes with dithizone as compared to the Hg²⁺.

3.3. Effect of temperature

The adsorption of Hg (II) onto GBP at different temperatures showed an increase in the adsorption capacity with increase in temperature. The adsorption capacity varied with temperature as shown in Fig. 3. With increase in temperature from 303 to 323 K, the adsorption capacity increased from 3.272 to 3.364 mg g⁻¹ for the initial concentration of 50 mg L⁻¹ at pH 9.0. Similar trends were observed for other concentrations also. This indicated that the adsorption reaction was endothermic in nature. The enhancement in the adsorption capacity was due to the chemical interaction between adsorbate and adsorbent, creation of some new adsorption sites as studied by Asku et al. [22]. The change in standard Gibbs free energy (ΔG^0), standard enthalpy (ΔH^0) and standard entropy (ΔS^0) were calculated by using the following equations,

$$\Delta G^0 = -RT \ln K_C \quad (2)$$

$$\Delta H^0 = R \left[\frac{T_1 T_2}{T_2 - T_1} \right] \ln \frac{K_{C2}}{K_{C1}} \quad (3)$$

$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T} \quad (4)$$

where K_C , K_{C1} and K_{C2} are equilibrium constant at temperatures T , T_1 and T_2 , respectively.

The negative values of ΔG^0 reflected the feasibility of the process and the positive values of ΔH^0 indicated the endothermic adsorption process. Standard entropy determined the disorderliness of

Table 2

Thermodynamic parameters of GBP at initial concentration 40 mg L⁻¹, pH 9.0

T (K)	ΔG^0 (kcal mol ⁻¹)	ΔH^0 (kcal mol ⁻¹)	ΔS^0 (cal mol ⁻¹ K ⁻¹)
303	-0.3359	1.067	4.6306
313	-0.3822	0.9101	4.1289
323	-0.4235		

the adsorption at solid–liquid interface. Table 2 summarizes the results.

3.4. Adsorption kinetics

The kinetics of adsorption describes the rate of uptake of Hg (II) onto GBP and this rate controls the equilibrium time. This study revealed that 60–70% of the adsorption had taken place in the first hour of contact. The amount of metal ions removed in the first hour of contact increased with increase in metal ion concentrations. The effect of temperature on the uptake rate of metal ions showed that rate of removal increased with increase in temperature. The kinetics of Hg (II) onto GBP was analysed by pseudo second-order mechanisms at different temperatures. The experimental data and calculated data were compared based on the regression coefficient (R^2) are shown in Table 3.

The pseudo second-order model can be represented as,

$$\frac{t}{q_t} = \frac{1}{k} + \frac{t}{q_e} \quad (5)$$

where t is time (min), q_t (mg g⁻¹) and q_e (mg g⁻¹) are amount of Hg (II) adsorbed at time t , equilibrium time, respectively, k

Table 3

Adsorption kinetics rate constant at different temperatures

T (K)	c_0 (mg L ⁻¹)	q_e (exp) (mg g ⁻¹)	k (g mg ⁻¹ min)	q_e (cal) (mg g ⁻¹)	R^2
303	30	1.814	0.2561	1.935	0.999
	40	2.513	0.3972	2.688	0.998
	50	3.268	0.6608	3.437	0.999
313	30	1.866	0.3163	1.979	0.999
	40	2.596	0.6075	2.696	0.999
	50	3.324	0.8154	3.463	0.999
323	30	1.908	0.3705	2.007	0.999
	40	2.637	0.6858	2.740	0.999
	50	3.364	1.0540	3.469	0.999

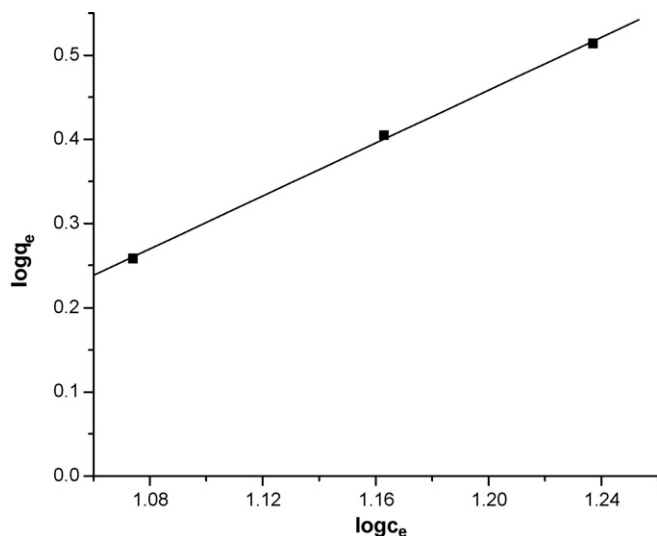


Fig. 4. Freundlich adsorption isotherm at pH 9.0 and $T = 303$ K.

Table 4

Adsorption isotherm at different temperatures

T (K)	Freundlich constants		R^2
	K_F	n	
303	0.2394	0.635	0.999
313	0.2761	0.676	0.999
323	0.3092	0.713	0.999

($\text{g mg}^{-1} \text{ min}$) is the second-order rate constant. The calculated q_e values agreed very well with experimental values and regression coefficient of above 0.99 confirmed that the adsorption phenomena followed second-order kinetics.

3.5. Adsorption isotherm

Adsorption equilibrium data were fitted to Freundlich isotherm at various temperatures. Freundlich isotherm shown in Fig. 4 describes the heterogeneous surface energies by monolayer adsorption and is expressed in linear form as,

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (6)$$

where K_F and n are Freundlich constants which is correlated to the maximum adsorption capacity and adsorption intensity, respectively. For the range $0.1 < n < 1$ adsorption is favourable. Increase in Freundlich constants with temperature confirmed the endothermic nature of adsorption. The theoretical parameters of isotherms with regression coefficients (R^2) are listed in Table 4.

4. Conclusion

Under batch conditions, equilibrium was attained within 80 min. Increase in adsorption capacity with increase in temper-

ature reveals that the adsorption is chemical in nature and the process is endothermic, which is confirmed by the thermodynamic parameters evaluated. The Hg (II) uptake followed second-order kinetics. Easy availability and suitability of the guava bark powder makes it one of the bioadsorbent that can be effectively utilized for the removal of Hg (II) from aqueous solutions.

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