Adsorption of mercury (II) ion from aqueous solution using low-cost activated carbon prepared from mango kernel

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ABSTRACT: A low-cost activated carbon (AC) was prepared from mango kernel through chemical activation with ZnCl2. The adsorption capacity of AC was investigated for the removal of Hg(II) from aqueous solution as batch experiments using varying initial adsorbent dosage, pH, equilibrium time and temperature. The prepared AC had a Brunauer-Emmett-Teller surface area of 920 m²g⁻¹ and total pore volume of 0.341 cm³g⁻¹, respectively. A maximum removal of 92% was achieved with an initial Hg(II) concentration of 10 mg L⁻¹, pH 6.5 and adsorbent dose of 3 g L⁻¹. The obtained kinetic experimental data were fitted to pseudo-first-order, pseudo-second-order and intraparticle diffusion models, respectively. Among the models, the pseudo-second-order adsorption model was found to be better, with a coefficient of regression (R²) > 0.95. The equilibrium data were also fitted to the Langmuir and Freundlich equilibrium isotherm models. Both the models were found to provide a better fitting with coefficient of regression (R²) > 0.98. The enthalpy of adsorption was found to be 7.2 kJ mol⁻¹. © 2012 Curtin University of Technology and John Wiley & Sons, Ltd.

Keywords: activated carbon; adsorption kinetics; Hg(II); mango kernel; adsorption isotherms

INTRODUCTION

The problems of the ecosystem are increasing because of the uncontrolled discharge of the industrial effluent to the aquatic environment. Most of the heavy metals containing effluents pollute the water bodies. Some heavy metals are necessary for the growth of plants, beyond certain concentrations become lethal to flora, fauna and microbes. Thus, bioaccumulation leads to food poisoning in human beings and animals. Presence of heavy metals in the aquatic environment has been of great concern to scientists and engineers because of their increased discharge, toxic nature and other adverse effects on receiving waters. Therefore, removal of heavy metals becomes mandatory. Moreover, it was observed that among all the heavy metal ions, Hg(II) stands on the top of toxicity severity list.[11] In addition to it, one of the dominant problems of Hg(II) is bioaccumulation in food chain.[22] It also leads to greater risk of chronic poisoning of endocrine system, reduced fertility, slower growth and development, and abnormal behavior that affects survival,[3,4] even if environmental levels of the toxin are not very high. Industries responsible for the discharge of mercury include chlor-alkali, paint, pulp and paper, oil refining, electrical, rubber processing, and fertilizer.[1]

According to the USA’s Environmental Protection Agency, permissible limit of mercury in wastewater is 0 mg/L, and for Bureau of Indian Standards, it is 0.01 mg/L. Hence, the removal of mercury from the aquatic environment has become a great concern. The general practice to remove mercury from aqueous solution include solvent extraction,[5] solid-phase extraction using silica derivatives,[6] commercial activated carbon (AC),[7] biosorbents,[8] sol–gel materials,[9] agro-based waste materials,[10] chitosan[11] and other materials.[12–15] Although all these methods yield better removal, they are not economical and lack selectivity too. Hence, adsorption with low-cost adsorbents has been widely used for removal of heavy metals from wastewater. Owing to its better selectivity and regeneration capacity, it could be a better alternative to replace the widely used commercial AC. In addition, they are cheaper and prepared from an alternative material like agricultural waste, bio-waste, etc.[16–26] Low-cost sorbents prepared from coal fly ash,[27] coffee grounds,[28] bagasse, cashew nut shell, palm shell kernel, coconut shell, etc. has been studied extensively to remove heavy metals from wastewater. Similarly in the present study, mango kernel, an agricultural waste, was selected as precursor for preparation of AC for the removal of mercury ion. Disposal of mango waste is a
major issue in a country like India. Annually, millions of mango kernels are produced as waste, and they are arbitrarily discarded or burned. Such disposals result in serious environmental pollution. Few researchers have experimented with mango kernel as adsorbent for removal of pollutants from aqueous solution. Vasanth Kumar and Kumaran studied the removal of methylene blue using mango kernel powder without activation. Gonzalez and Montoya investigated the prepared carbonaceous mango seed adsorbents in the adsorption of antracquinone and azo acid dyes in single and binary aqueous solutions. They studied that the husk of the mango seed can be used as a good adsorbent, and the adsorption efficiency was dependant not only on the chemical and textural characteristics of the adsorbent. Studies on evaluating the adsorption potential of heavy metal on chemically AC prepared from mango kernel are scant. Hence, the present study aimed in preparing a chemically AC using mango kernel, and its adsorption potential, kinetics, thermodynamics and sorption equilibrium were studied for the removal of a mercury ion.

MATERIALS AND METHODS

Materials

All the chemicals were purchased from Loba Chime Pvt. Ltd. India as analytical grade and used without further treatment. Ethylenediaminetetraacetic acid (EDTA), acetate buffer, phenanthroline, gelatin and eosin solutions were used as reagents for determination of Hg(II) using spectrophotometric analysis. ZnCl₂ (AR grade) was used as activating agent for mango kernel.

Preparation and characterization of adsorbent

Mango kernels were washed with distilled water to remove dirt and other contaminants and oven-dried at about 110°C for 24 h. The dried seeds were crushed in the ball mill and sieved to obtain the desired size fractions. Desired size material was washed with distilled water once again and then dried in oven at about 110°C for 24 h. The dried sample of 40 g was mixed with 200 mL of aqueous solution of 20% ZnCl₂ (wt/wt). The impregnated sample was placed in a tubular muffle furnace. The activation was carried out at 600°C under an inert flow of N₂ gas for 2 h for carbonization and then treated with 0.1 mol dm⁻³ HCl at room temperature for 24 h to remove residual organic and mineral matters. The samples were then vacuum-dried at 102°C. Finally, the vacuum dried material was stored in desiccators filled with N₂ gas to prevent oxidation.

Scanning electron microscopic photographs were recorded without sample coating using scanning electron microscope. The micrographs and Energy-dispersive X-ray spectroscopy (EDAX) were taken with a scanning electron microscope (Zeiss AURIGA® 60). N₂ adsorption–desorption isotherms were measured with Micromeritics ASAP 2020 Surface Area and Porosity Analyzer V3.00. Prior to analysis, the samples were outgassed at 150°C for 12 h. The pore-size distribution curves were obtained from the analysis of the desorption portion of the isotherms using the Barrett-Joyner-Halenda (BJH) method, and the total pore volume was estimated at a relative pressure of 0.99, assuming full surface saturation with nitrogen. The surface area was calculated using a multipoint Brunauer-Emmett-Teller (BET) model. Fourier transform infrared spectroscopic spectra were recorded between 4000 and 500 cm⁻¹ region using spectroscopic quality KBr powder with Perkin-Elmer spectrum RXI model.

Batch adsorption studies

Adsorption studies were carried out as batch experiments. A stock solution [1000 mg L⁻¹ Hg(II) ions] was prepared by dissolving 0.3385 g of mercuric chloride in distilled water and diluted to 250 mL. Experimental solutions of the desired concentrations were attained by successive dilutions with distilled water. Experiments were carried out in 100-mL Erlenmeyer flask with 50 mL of Hg(II) aqueous solution by adding known weight of the prepared AC from mango kernel. The contents of mixture were agitated in a temperature-controlled reciprocating shaker (ORBITEK LSO-30) at a constant speed of 200 rpm at 30°C±1°C. Samples were withdrawn at appropriate time intervals and filtered through Whatman® filter paper. The residual concentration of mercury was determined spectrometrically. Blank experimental runs, with only the adsorbents in 50 mL of distilled water, were conducted simultaneously using filter paper at similar conditions to account for mercury ions. The initial pH (pH₀) of the solution was adjusted by adding dilute aqueous solution NaOH and HCl (0.1 M). The adsorption experiments were also carried out to determine the equilibrium time, the optimum pH, temperature and dosage of the adsorbent for maximum adsorption. The amount of mercury ion adsorbed on AC was obtained using Eqn (1):

\[ q_t = \frac{(C_o - C_t)V}{m} \] (1)

Where \( q_t \) is the amount of Hg(II) adsorbed at time \( t \) (mg L⁻¹); \( C_o \) and \( C_t \) are the initial and at any time \( t \) concentrations of Hg(II) ion in aqueous solution, respectively, computed from calibration curve; \( V \) is the volume of the solution (L); and \( m \) is the mass of the adsorbent (g).

Kinetic and isotherm studies

The kinetic study was carried out by introducing quantities of 0.1 g of AC into 50 mL of Hg(II) solutions at
various initial concentrations from 10 to 100 mg L\(^{-1}\); the samples were collected at known intervals of time and analyzed. For adsorption, isotherm experiments were performed with 50 mg L\(^{-1}\) of Hg(II) initial concentrations by varying at different adsorbent dosages of 0.05, 0.1 and 0.15 g, agitated till the equilibrium was attained. The residual concentration of mercury ion was determined.

**Mercury determination**

A sample solution containing residual of Hg(II) ions was mixed with 1 mL of 0.05 M EDTA solution, 5 mL of acetate buffer (pH 4.5), 2 mL of \(2.5 \times 10^{-3}\) M 1, 10-phenanthroline solution and 1 mL of freshly prepared gelatin solution. The solutions were mixed thoroughly, and then 5 mL of \(7.3 \times 10^{-4}\) M eosin solution was added. The contents were again mixed well and diluted to the mark in 25-mL volumetric flasks with Milli-Q water. The absorbance of the samples is measured in 10-mm cell at 552 nm against blank. Concentrations of Hg(II) were determined by finding out the absorbance at the characteristic wavelength (\(\lambda_{\text{max}}\)) using a UV/Vis spectrophotometer.[33]

**RESULTS AND DISCUSSION**

**Characterization of adsorbent**

Chemical composition of the AC prepared was analyzed with EDAX. From Fig. 1, the pore development owing to chemical activation of AC can be observed from the surface morphology. It can be seen from the micrographs that the external surface of the chemically AC is full of cavities, exhibiting a heterogeneous structure in terms of both size and shape. The EDAX spectrum of the sample is shown in Fig. 1, where it is confirmed that carbon dominates with a weight percentage of 91, whereas N, O, Zn, and Cl are in the order of 0.96%, 2.13%, 1.98%, and 3.77%, respectively. That carbon is found to be dominant over other element confirms that the prepared material should have well-adsorbent properties.

The Fourier transform infrared spectroscopic spectra of the AC prepared from mango kernel treated using chemical activation are shown in Fig. 2. The spectrum of sample treated with 20% ZnCl\(_2\) indicated the presence of hydroxyl, carboxyl, carbonyl, amino and nitro groups, which are important sorption sites. In order to understand the surface binding mechanism, it is essential to identify the functional groups present on the adsorbent involved in this process. The strong band in the region, 3416 cm\(^{-1}\), is significant and indicative of the existence of stretching O-H vibrations. The absorption peak at 1564 cm\(^{-1}\) was assigned to C-C stretch in ring indicating the presence of aromaticity. The moderate absorption peaks at 1028 cm\(^{-1}\) can be assigned to the band of the C-O stretching. The similar results were observed in the carbon from cherry stones and guava obtained.[34,35]

The BET surface area, micropore volume, mesopore volume, Density Functional Theory (DFT) pore volume and average pore width of AC were investigated. Identifying the pore structure of adsorbents, commonly determined using the adsorption of inert gases, is an
essential procedure before liquid sorption. Fig. 3 shows the typical adsorption/desorption isotherms of N₂ at -196 °C for the AC. The micropore size distribution was obtained using the BJH method as shown in Fig. 3b. The micropore size estimated from the Horvath–Kawazoe method is shown in Fig. 3c. From Fig. 3, it can be inferred that maximum pore volume is obtained within the radius range of (0–2) nm. It can be observed that at a pore width of 0.8248 nm, the gradient of differential pore volume becomes zero indicating that the pore volume is at maximum at this point. The surface area and total pore volume of the AC is found to be 920 m² g⁻¹ and 0.341 cm³ g⁻¹, respectively.

**Batch adsorption study**

**Effect of contact time**

Effect of contact time for removal of Hg(II) using prepared AC was studied at various initial Hg(II) concentrations of 10, 20, 30, 40 and 50 mg L⁻¹ and adsorbent dosage of 2 g L⁻¹ in order to determine the equilibrium time for maximum adsorption capacity. The results indicate that the rate of Hg(II) removal progressively decreased with increasing time. Approximately, it took 3 h to reach the equilibrium adsorption. Therefore, the equilibration time was set conservatively at 3 h for further experiments.

The adsorption rate was very fast initially; 50% of adsorption for all the concentrations was reached in less than an hour, and consequently, the extent of ion uptake decreases significantly by increasing contact time, depending on the reduction rate of vacant sites on the adsorbent surface (Fig. 4). The removal of Hg(II) produced single, smooth and continuous curves leading to saturation. The adsorption curve with respect to time indicates the possible monolayer coverage of Hg(II) on outer surface of adsorbent.

**Effect of adsorbent dosage**

The effects of adsorbent dosage on the percentage removal of Hg(II) using AC at initial concentration of Hg(II) 50 mg L⁻¹, pH₀ = 6.5 and temperature of 303 K were studied for different dosages of 0.05, 0.075, 0.1, 0.125 and 0.15 g in 50-mL solution. Figure 5 shows that the percentage removal of Hg(II) has increased with increase in the adsorbent dosage; however, the amount adsorbed decreased from 14.52 to 8.82 mg g⁻¹.

**Figure 3.** N₂ adsorption–desorption isotherms. (a) Pore size distribution and (b) differential pore volume plot of (c) prepared AC.

**Figure 4.** Effect of contact time on the percentage removal of Hg(II) using AC (T = 303 K, m = 0.1 g, pH₀ = 6.5).
as the dosage varied from 0.05 to 0.15 g, respectively. This could be attributed to the fact that the number of available adsorption sites increased with an increase in adsorbent dosage. The decrease in adsorption capacity with an increase in the adsorbent dosage could be ascribed to the fact that some of the adsorption sites remained unsaturated during the adsorption process. Another reason could be probably because of the interparticle interaction, such as aggregation, resulting from high adsorbent concentration. Such aggregation would lead to a decrease in the total surface area of the adsorbent and an increase in the diffusion path length.\[38\]

**Effect of initial Hg(II) concentration**

Figure 6 depicts the effect of initial concentration on the percentage removal of Hg(II) and equilibrium concentration in the adsorbent phase using AC. The amount of adsorption increased per unit mass of adsorbent, and the percentage of Hg(II) removal decreased with the increase in initial Hg(II) concentration. As initial Hg(II) concentration increased from 10 to 100 mg L\(^{-1}\), the adsorption capacity of Hg(II) on the AC increased from 4.4 to 15.51 mg g\(^{-1}\). The initial Hg(II) concentration provided the necessary driving force to overcome the resistances to the mass transfer of Hg(II) between the aqueous and the solid phases. The increasing concentration also enhanced the interaction between Hg(II) and AC. Therefore, the adsorption of Hg(II) increased. The percentage removal of Hg(II) decreased from 88% to 31% with increase in initial Hg(II) concentration because the adsorbent dosage is fixed (0.1 g). So the number of active sites for adsorption is decreasing with increase in \(C_0\).

**Effect of initial pH**

The initial pH of the metal ion solution plays an important role in the whole adsorption process and particularly on the adsorption capacity. Figure 7 shows the effect of pH on the amount of Hg(II) adsorbed on adsorbent of 0.1 g at initial concentration of 50 mg L\(^{-1}\) and temperature of 303 K. Increasing the pH of the metal ion solution in the absence of carbon did not precipitate Hg(II) as metal hydroxide using hydrolysis owing to the formation of chloride complexes of Hg (II): HgCl\(^+\), HgCl\(_2\), HgCl\(_3\) and HgCl\(_4^{2-}\). The chloride ion effectively decreases the degree of hydrolysis of Hg(II) ion by blocking some of the coordination positions.\[39\] From these reactions, it is possible to generate three uncharged species—HgCl\(_2\), HgCl(OH) and Hg (OH)\(_2\)—all of which are linear and probably exist in natural water systems. The removal of Hg(II) was observed over a range of pH\(_o\) values between 2 and 10 using AC. The percentage of mercury removal increases with increasing initial solution pH. The influence of pH\(_o\) on Hg(II) removal may be explained as follows: in the acidic condition, both the adsorbent and the adsorbate are positively charged (M\(^{2+}\) and
H\textsuperscript{+}), and therefore, the net interaction is that of electrostatic repulsion.\textsuperscript{[40]} Besides, the higher concentration of H\textsuperscript{+} ions present in the reaction mixture competes with the positively charged Hg(II) ions for the surface adsorbing sites, resulting in a decrease in the removal of Hg(II). Kadirvelu\textsuperscript{[41]} has reported a similar kind of effect for the adsorption of Hg(II) from aqueous solution using coir pith carbon.

**Effect of temperature**

Temperature has a pronounced effect on the adsorption capacity of the adsorbents. The percentage removal of Hg(II) with respect to initial concentrations of 10–50 mg L\textsuperscript{-1} using 0.1 g of adsorbent dose at different temperatures ranging from 303 to 323 K was studied. From Fig. 8, it is evident that the mercury removal percentage increases with increase in temperature. The increase in adsorption capacity with increase in temperature indicates that some kind of chemical interaction between metal ion and adsorbent may take place during adsorption process.\textsuperscript{[42]} This process is endothermic in nature; therefore, at higher temperatures, the rate of intraparticle diffusion of adsorbate ions into the pores increases. The results of the present investigation on temperature effect also support the conclusion that Hg(II) sorption is controlled by pore diffusion.

**Adsorption kinetic study**

In order to investigate the adsorption kinetics of Hg(II) using AC at different initial Hg(II) concentration at fixed amount of adsorbent at 0.1 g, temperature of 303 K and pH\textsubscript{o} 6.5 using pseudo-first-order, pseudo-second-order and intraparticle diffusion kinetic models.

**Pseudo-first-order model**

A simple kinetic analysis of adsorption was the Lagergren or pseudo-first-order Eqn (2).\textsuperscript{[43]}

$$\frac{dq_t}{dt} = k_1(q_e - q_t)$$  \hspace{1cm} (2)

Where \(q_t\) was the amount of adsorbate adsorbed at time \(t\) (mg g\textsuperscript{-1}), \(q_e\) was the adsorption capacity at equilibrium (mg g\textsuperscript{-1}), \(k_1\) was the pseudo-first-order rate constant (min\textsuperscript{-1}) and \(t\) was the contact time (min). After definite integration, by applying the initial conditions \(q_t = 0\) at \(t = 0\) and \(q_t = q_e\) at \(t = t\), Eqn (2) becomes

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right)t$$  \hspace{1cm} (3)

The slope and intercepts of the plots of \(\log(q_e - q_t)\) vs \(t\) determined the first-order rate constant, \(k_1\) and equilibrium adsorption capacity \(q_e\) for different initial Hg(II) concentrations. A comparison of the results with the correlation coefficients is shown in Table 1. The correlation coefficients for the first-order kinetic model obtained at all the studied concentrations were low. Also, the theoretical \(q_e\) values found from the first-order kinetic model did not give reasonable values. Thus, it confirms that the studied adsorption system does not follow first-order reaction.

**Pseudo-second-order model**

In addition, a pseudo-second-order\textsuperscript{[43]} based on adsorption equilibrium capacity may be expressed in the form of Eqn (4):

$$\frac{dq_t}{dt} = k_s(q_e - q_t^2)$$  \hspace{1cm} (4)

Where \(k_s\) was the pseudo-second-order rate constant (gm g\textsuperscript{-1} min\textsuperscript{-1}). Integrating Eqn (2) and applying the initial conditions \(t = 0\) and \(q_t = 0\) to \(t = t\) and \(q_e = q_r\), Eqn (5) was obtained:

$$\frac{t}{q_t} = \frac{1}{k_s q_e^2} + \frac{t}{q_e}$$  \hspace{1cm} (5)

The slopes and intercepts of plots \(t/q_t\) vs \(t\) were used to calculate the second-order rate constants \(k_2\) and \(q_e\). Figure 9 shows that a straight line plot of \(t/q_t\) vs \(t\) confirms that obtained experimental data had good agreement with the second-order kinetic model for different initial Hg(II) concentrations. Table 1 lists the computed results obtained from the second-order kinetic model. The coefficient of regression (\(R^2\)) for the second-order kinetic model obtained was >0.99 for all concentrations. The calculated \(q_e\) values also agree very well with the experimental data. Thus, it revealed that the studied adsorption system strongly follows second-order kinetic model.

![Figure 8](image-url)  \hspace{1cm} Figure 8. Effect of temperature on the percentage removal of Hg(II) using AC \((m = 0.1\ g,\ t = 3\ h,\ \text{pH}_o = 6.5)\).
Intraparticle diffusion

The possibility of intraparticle diffusion was explored by using the intraparticle diffusion model:

\[ q_t = k_{id} t^{1/2} + I \]  

(6)

Where \( k_{id} \) was the intraparticle diffusion rate constant (mg g\(^{-1}\) min\(^{-1/2}\)) and \( I \) is the intercept (mg g\(^{-1}\)). According to Eqn (4), a plot of \( q_t \) vs \( t^{1/2} \) should be a straight line with a slope \( k_{id} \) and intercept \( I \) when adsorption mechanism follows the intraparticle diffusion process. Figure 10 illustrates plot of \( q_t \) vs \( t^{1/2} \) for the adsorption of Hg(II) using prepared AC. Two separate regions was observed: the initial portion is attributed to the bulk diffusion and the linear portion is attributed to intraparticle diffusion. The values of \( k_{id,1} \) and \( k_{id,2} \) as obtained from the slopes and \( I_1 \) and \( I_2 \) as obtained from intercepts of the two straight lines were listed in Table 1.

![Figure 9. Pseudo-second-order kinetics for Hg(II) from aqueous solution using AC at various initial concentration (m = 0.1 g, T = 303 K, pH\(_o\) = 6.5).](image)

![Figure 10. Intraparticle diffusion plot of Hg(II) onto AC at various initial concentrations (m = 0.1 g, T = 303 K, pH\(_o\) = 6.5).](image)
Adsorption equilibrium study

To optimize the design of system for the adsorption of adsorbates, it was important to establish the most appropriate correlation for the equilibrium curves. Various isotherm equations like Freundlich, Langmuir and Temkin were used to describe the equilibrium characteristics of adsorption. The Freundlich isotherm was derived by assuming a heterogeneous surface with a nonuniform distribution of heat of adsorption over the surface. Whereas in the Langmuir theory, the basic assumption was that the sorption takes place at specific homogeneous sites within the adsorbent.

**Langmuir isotherm**

In the Langmuir theory,\(^4\) the basic assumption is that the sorption takes place at specific homogeneous sites within the adsorbent.

\[
q_e = \frac{K_L C_e}{1 + a_l K_L C_e} \quad (7)
\]

Where \(C_e\) is the equilibrium concentration (mg L\(^{-1}\)), \(q_e\) is the amount of Hg(II) sorbed at equilibrium (mg g\(^{-1}\)), the constant \(K_L\) is the Langmuir equilibrium constant and the \(K_L/a_l\) gives the theoretical monolayer saturation capacity, \(Q_o\). The linearized form of Langmuir isotherm can be written as follows.

The equilibrium data for adsorption of Hg(II) over the concentration range from 10 to 100 mg L\(^{-1}\) at 30\(^\circ\)C have been correlated with the Langmuir isotherm. The Langmuir constants \(Q_o\) and \(K_L\) were calculated from the slope and intercept of plot between \(C_e/q_e\) vs \(C_e\) in Fig. 11. The Langmuir model parameters and regression of fits of the sorption data to this equation are tabulated in Table 2.

**Freundlich isotherm**

The Freundlich isotherm\(^4\) is derived by assuming a heterogeneous surface with a nonuniform distribution of heat of adsorption over the surface

\[
q_e = K_F C_e^{1/n} \quad (9)
\]

Where \(C_e\) is the solute concentration in the liquid at equilibrium (mg L\(^{-1}\)), \(q_e\) is the amount of Hg(II) sorbed at equilibrium (mg g\(^{-1}\)) and \(K_F\) (mg g\(^{-1}\)) and \(n\) are the Freundlich constants related to adsorption capacity and adsorption intensity. The linearized form of Freundlich isotherm can be written as follows:

\[
\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (10)
\]

The Freundlich constant \(K_F\) and \(n\) can be calculated from the intercept and slope of plot between \(\log q_e\) and \(\log C_e\) shown in Fig. 12. The Freundlich constants \(K_F\) and \(n\) and correlation coefficients are presented in Table 2. \(n\) is a characteristic constant for the adsorption system and if its value lies between 2 and 10, it indicates good adsorption. In the present study, the value of \(n\) varied between 3 and 5, which indicates that the adsorption capacity is only slightly suppressed at lower equilibrium concentrations. The value of correlation coefficient is higher (>0.98) than the other two isotherm values. Thus, the Freundlich equation shows best fit of experimental data over Langmuir.

**Temkin isotherm**

The Temkin isotherm equation represented as in Eqn (11):

\[
K_T = \frac{R T}{q_e} \ln C_e \quad (11)
\]

Where \(C_e\) is the equilibrium concentration and \(\ln C_e\) is the slope of the plot. The Temkin isotherm parameters and regression of fits of the sorption data to this equation are tabulated in Table 2.

**Table 2. Isotherm parameters for the adsorption of Hg(II) over AC (\(C_o = 10–100\) mg L\(^{-1}\), \(T = 303\) K, \(t = 3\) h, pH\(_o\) = 6.5).**

<table>
<thead>
<tr>
<th>Adsorbent dose (g)</th>
<th>Langmuir isotherm</th>
<th>Freundlich isotherm</th>
<th>Temkin isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(K_L)</td>
<td>(Q_o)</td>
<td>(R^2)</td>
</tr>
<tr>
<td>0.05</td>
<td>0.153</td>
<td>19.762</td>
<td>0.98</td>
</tr>
<tr>
<td>0.1</td>
<td>0.187</td>
<td>15.984</td>
<td>0.98</td>
</tr>
<tr>
<td>0.15</td>
<td>0.124</td>
<td>12.626</td>
<td>0.97</td>
</tr>
</tbody>
</table>

This can be linearized as:

\[ q_e = \frac{RT}{b} \ln(K_T C_e) \]  

(11)

This can be linearized as:

\[ q_e = B_1 \ln(K_T) + B_1 \ln(C_e) \]  

(12)

Where

\[ B_1 = \frac{RT}{b} \]  

(13)

Temkin isotherm contains a factor that explicitly takes into the account adsorbing species–adsorbent interactions. This isotherm assumes that (i) the heat of adsorption of all the molecules in the layer decreases linearly with coverage because of adsorbent–adsorbate interactions and that (ii) the adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy.\(^{[44]}\) A plot of \(q_e \text{ vs } \ln C_e\) enables the determination of the isotherm constants \(B_1\) and \(K_T\) from the slope and the intercept in Fig. 13, respectively. The values of the Temkin constants \(K_T\) and \(B_1\) and correlation coefficient are listed in Table 2. \(K_T\) is the equilibrium binding constant (L mol\(^{-1}\)) corresponding to the maximum binding energy, and constant \(B_1\) is related to the heat of adsorption. The model parameters from all isotherms obtained were presented in Table 2. From Table 2, it is clear that the Langmuir and Freundlich models had a better fit with a good \(R^2\) value than Temkin isotherm model.

**Estimation of thermodynamic parameters**

Thermodynamic considerations of adsorption process are essential to conclude whether the process is spontaneous or not. The thermodynamic parameters, namely free energy (\(\Delta G^o\)), enthalpy (\(\Delta H^o\)) and entropy (\(\Delta S^o\)), have an important role to determine spontaneity and heat change of the adsorption process. Equilibrium constant can be used to evaluate the thermodynamic parameters.\(^{[45]}\)

The change in Gibbs free energy of the process is related to the equilibrium constant by the following equation

\[ \Delta G^o = -RT \ln K_o \]  

(14)

where \(K_o = C_{wed}/C_e\), \(K_o\) is the equilibrium constant.

The enthalpy change \(\Delta H^o\) and the entropy change \(\Delta S^o\) were obtained from Eqn (12):

\[ \ln K_o = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{R} \left( \frac{1}{T} \right) \]  

(15)

\(\Delta H^o\) and \(\Delta S^o\) can be obtained from the slope and intercept of the van’t Hoff’s plot of \(\ln K_o\) vs \(1/T\) as shown in Fig. 14. The negative values of \(\Delta G^o\) suggest

![Figure 12. Freundlich adsorption isotherm for Hg(II) adsorbed using AC different amount dosage \((C_o = 10-100 \text{ mg L}^{-1}, T = 303 \text{ K}, \text{pH}_o = 6.5, t = 3 \text{ h})\).](image1)

![Figure 13. Temkin isotherm for Hg(II) adsorbed using AC at different amount dosage \((C_o = 10-100 \text{ mg L}^{-1}, T = 303 \text{ K}, \text{pH}_o = 6.5, t = 3 \text{ h})\).](image2)

![Figure 14. van’t Hoff plot of Hg(II) adsorption on prepared AC.](image3)
the feasibility of the process. It was observed that the values become more negative with increase in temperature. An increase in $\Delta G$ with temperature suggests high adsorption of Hg(II) at lower temperatures. The values of $\Delta S^0$ and $\Delta H^0$ are 37.0388 J mol$^{-1}$ K$^{-1}$ and 7.510 J mol$^{-1}$ K$^{-1}$, respectively. The positive values of $\Delta H^0$ for Hg(II) adsorption indicate that the reaction is endothermic nature. The endothermic process shows that diffusion from bulk solution to adsorbent interface may require energy to overcome interaction of dissolved ions with dissolution molecules. The positive value of $\Delta S^0$ (Table 3) shows the increased disorder and randomness at the solid solution interface during the adsorption of metal ion. A similar observation reported was observed for Hg(II) adsorption on bagasse pith by Krishnan and Anirudhan.[42]

### CONCLUSIONS

The AC prepared from mango kernel using chemical activation was successfully employed for the adsorption of Hg(II). The adsorption equilibrium between the adsorbate and the adsorbent surface was achieved in 3 h. The percentage removal of metal ion adsorbed was found to vary marginally with initial solution pH, adsorbent dose, contact time and temperature. The mercury removal efficiency found to increase with increase in initial pH, adsorbent dose and temperature. The adsorption followed pseudo-second-order model and dominantly by a two-step intraparticle diffusion process. The studied adsorption process also best fitted with Freundlich equilibrium model than that of Langmuir and Temkin model. Thermodynamic study indicates that the adsorption process is endothermic in nature because of positive value of enthalpy change. Overall, the study revealed the potential of mango kernel AC as a better alternative in removing heavy metals completely from wastewater.

### REFERENCES


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