Modified Mangosteen Shell in the Removal of Hg (II) from Aqueous Solution-Isotherm and Kinetic Studies

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ABSTRACT

An activated carbon was prepared from an agricultural waste *mangosteen shell* by chemical modification (BTMC) and removal efficiency was tested using aqueous solution of Hg (II). The functional groups and surface morphology of BTMC were analyzed using FT-IR and SEM studies. Commercial activated carbon (CAC) was used to compare the efficiency of BTMC in Hg (II) removal. Batch mode studies were conducted to evaluate the parameters like contact time, pH, carbon dose on the removal efficiency of Hg (II) from aqueous solution. Removal of mercury occurs at optimal contact time of 120 min at pH 5 and carbon dosage of 120 mg for BTMC. Adsorption isotherm was studied using Freundlich, Langmuir, and Temkin isotherm models. Equilibrium data fitted well with Langmuir isotherm. The maximum adsorption capacity of Hg (II) was found to be 49.75 mg g^{-1} for BTMC. The pseudo second-order kinetic model fits well with the experimental data. Wastewater analysis was also performed to evaluate the practical applicability of the carbon.

Key words: adsorption, mangosteen shell, mercury, kinetics, isotherm

1. INTRODUCTION

Modern agricultural practices and the rapid growth of industries act as a major source of heavy metals in water bodies. Mercury is a toxic bioaccumulative and volatile poison. Mercury (II) finds its way into aquatic systems through wastes from paper and pulp industry, chloro-alkali plants, paint, pharmaceutical, rubber processing, smelting, burning of fossil fuels, oil refining, mining and battery manufacturing processes. As per WHO report the maximum permissible limit of mercury in drinking water is 0.001 mgL^{-1} [1,2].The US Environmental Protection Agency sets a Hg limit of 10 μgL^{-1} for wastewater discharge and 2 μgL^{-1} for drinking water [3]. Excessive Hg exposure may result in the development of symptoms such as tremors, loss of sensation in extremities, vision and hearing loss, or developmental and behavioural abnormalities [4]. Many conventional methods like chemical, oxidation and reduction, precipitation, ion exchange, coagulation, and adsorption are used for mercury removal. Due to low cost and efficient removal adsorption process is used by researchers for the removal of mercury from water. Agricultural wastes like rice husk[5]

terminalia catappa [6] palm shell [7] pea nutshell [8] wall nutshell [9] were used in the removal of mercury from water.

Mangosteen (Garcinia Mangostana Linn.) of Hypericaceae family is most commonly found in Asian countries Mangosteen shell which is available in plenty is used in the removal of heavy metal from water [10, 11].The phenolic acid present in the pericarp of mangosteen shell has the ability to bind heavy metals from the aqueous solution [12]. In the present investigation, chemical modification of mangosteen shell was done using sulphuric acid and tested for the removal efficiency of mercury from aqueous solution.

2. MATERIALS AND METHODS
2.1 Preparation of Carbon Adsorbent

Mangosteen shell collected from Thenkasi, India was washed with distilled water, dried at 110°C powdered and sieved to 20-50 ASTM mesh size. The dried material was treated with con H_2SO_4 (1:1) weight ratio and kept in a hot air oven at 150 ± 5°C for 24 h. The carbonized material was washed with distilled water to remove the free acid and soaked in 1% sodium bicarbonate until the effervescence ceases and further soaked in the same solution for 24 h to remove the residual acid. The activated carbon was washed with distilled water, dried at 105 °C and again sieved to 20-50 ASTM mesh size and labelled as Bicarbonate Treated Mangosteen Shell carbon (BTMC). The Commercial Activated Carbon (CAC) was also broken and sieved to 20-50 ASTM mesh size.

2.2 Preparation of Hg (II) Solution

A stock solution of Hg (II) (1000 mg L^{-1}) was prepared by dissolving 1.354 g of Hg_2Cl_2 solution in 1000 mL of distilled water. The solution was diluted as required to prepare standard solutions containing 10-50 mg L^{-1} of Hg (II).100 mL of Hg (II) solution of the desired concentration is adjusted to the desired pH using dilute hydrochloric acid solution or dilute sodium hydroxide solution.

2.3 Batch Adsorption Experiments

Adsorption studies were carried out by varying contact time (30-300 min), solution pH (1-10) and adsorbent dosage (40-320 mg).For each study a required quantity of adsorbent dose was added to 100 mL of 10 mg L^{-1} of Hg (II) solutions taken in polythene containers agitated in a mechanical shaker. The carbon was separated by filtration and the filtrate was analyzed by spectrophotometer using Rhodamine 6G reagent for Hg (II) content at 575 nm [13]. Adsorption isotherm studies were carried out with from aqueous solution. Commercial activated carbon obtained from Nice chemicals Pvt Ltd, India was used for comparative study.

3. RESULTS AND DISCUSSION

The characteristics of both the carbon were studied as per the standard procedure and observations listed in Table 1.

3.1 Fourier Transforms Infrared Spectroscopy Analysis

From the FTIR spectrum data of BTMC before and after Hg (II) adsorption it is evident that some of the peaks shift or disappear after adsorption indicating the incorporation of heavy metal ion Hg (II) within the adsorbent through the interaction of the active functional group after adsorption (Table 2)

3.2 SEM Analysis

The SEM image of the adsorbent BTMC before and after adsorption was shown in Figure 1(a, b).This microscope image shows the presence of isolated pores of varying dimension before and after adsorption. The cave- like opening before adsorption in BTMC is clearly seen and filled with Hg (II) ion after adsorption.

3.3 Effect of Contact Time

Equilibrium time is an important parameter to be analysed to study the adsorption process. Figure 2 shows the effect of contact time on the adsorption of Hg (II) on BTMC and CAC. The

Table 1. Characteristics of the carbon.

Parameter	BTMC	CAC
Bulk Density	0.54	0.71
Moisture (%)	3.14	2.28
Matter soluble in water (%)	5.12	1.58
Matter Soluble in 0.25M HCl (%)	16.31	2.04
pH	6.29	7.64
Decolorizing power (mg g^{-1})	12	5.1
Ion exchange capacity(m equiv g^{-1})	0.298	Nil
Surface area(m^2 g^{-1})	209	150
Porosity (%)	50.11	36.41

Table 2. FTIR spectral data of different functional groups before and after adsorption of Hg (II) on BTMC.

Frequencies(cm^{-1})		Corresponding functional groups
Before Adsorption	After Adsorption	
3425	3402	-OH stretching vibration
2981	Disappear	C-H stretching
2372	2364	C≡C stretching
1427	1435	Sulphonic acid
1222	Disappear	-CO stretching vibration of ether

results show that the removal of mercury ion increases with time and attains equilibrium in 120 min for BTMC and 210 min for CAC. Due to the presence of more uncovered area in the adsorbent initially, the adsorption is fast. As time increases the surface area are covered and the metal ion slowly diffuses into the intra-particular pore of the adsorbent.

At low pH value (pH 2), the number of negatively charged surface sites decreased and the number of positively charged sites increased, which did not favor the sorption of positively charged metal ions (Hg^{2+} and $Hg(OH)^+$) due to electrostatic repulsion. Additionally, lower adsorption of Hg (II) at acidic pH is due to the presence of excess H^+ ions competing with metal ions for the sorption sites. The increase in adsorption at pH 5 may be due to the less competition from protons to reaction sites, to an increase in concentration of $Hg(OH)^+$ species At higher pH

values the decrease in biosorption may be due to the formation of soluble hydroxilated compound ($Hg(OH)_2$).

3.4 Effect of pH

The removal of metal ion from aqueous solution by adsorption is highly dependent on the p^H of the solution. Figure.3 shows the effect of pH on the removal of Hg (II) by BTMC and CAC. It was observed that maximum removal of 87 % was observed for BTMC and 73 % for CAC at pH 5. Similar observations were reported for adsorption of moss, Ulva lactuca [14,15]

3.5 Effect of Carbon Dose

The effect of carbon dosage on the percentage removal of Hg (II) is shown in Figure 4. It was observed that initially, the percentage removal increases sharply with the increase in adsorbent dose but after 120 mg dose of BTMC and 210 mg dose
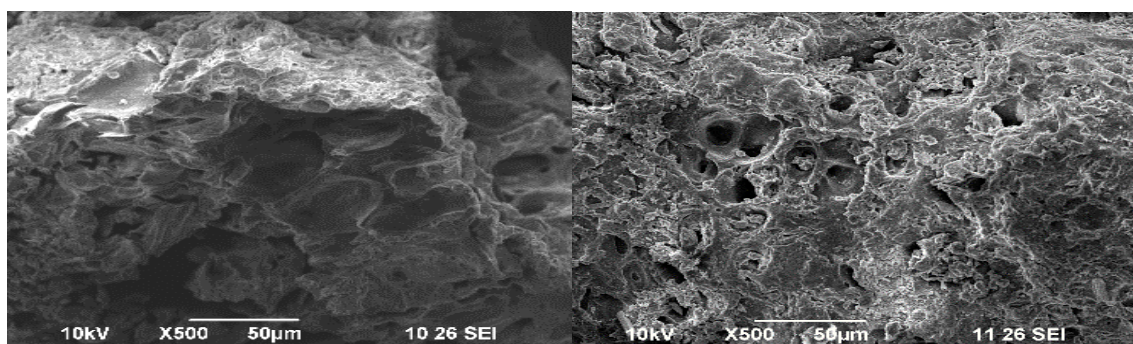
Figure 1. (a) SEM image of BTMC before adsorption **(b)** SEM image of BTMC after adsorption.
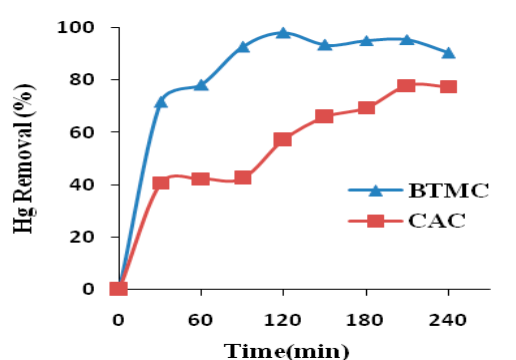

Figure 2. Effect of contact time on the removal of Hg (II) by BTMC and CAC.
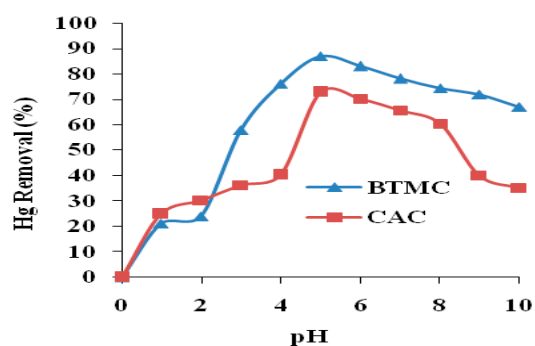

Figure 3. Effect of pH on the removal of Hg (II) by BTMC and CAC (Dose =100 mg/100 mL).

of CAC the percentage removal value is constant due to the reduction in a concentration gradient. The maximum removal efficiency of Hg (II) for BTMC and CAC are 99 % and 90% respectively. The increase in removal efficiency of Hg (II) ion may be due to the increase in adsorbent mass or availability of a large number of exchangeable sites for adsorption.
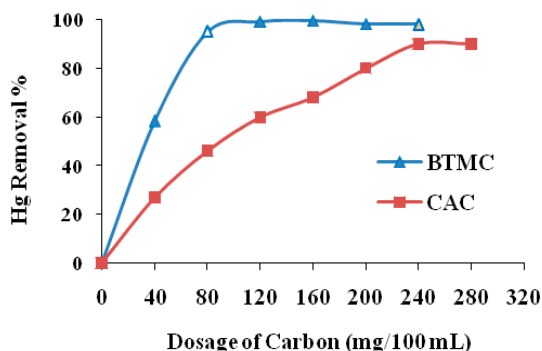
Figure 4. Effect of carbon dosage on the removal of Hg (II) by BTMC and CAC at (pH =5).

3.6 Effect of Temperature

The adsorption of Hg (II) was investigated at three different temperatures 27°C, 37°C, 47°C for the initial Hg (II) ion concentration of 10 mg L^{-1} at constant adsorbent dosage of 100 mgL^{-1} at optimum pH of 5.The % removal for is found to be 90%, 87%, 84% for BTMC and 60%, 52%, 47% for CAC. Maximum removal of Hg (II) was obtained at 27°C. The percentage removal of Hg (II) ion decreases with increase in temperature .This may be due to the decrease in surface activity of Hg (II). Similar observation were noted by Sudha et al and Huang et al [16,17]

3.7 Adsorption Isotherm

The adsorption isotherm was used to understand the equilibrium between the amount of adsorbate that accumulates on the adsorbent and the concentration of the dissolved adsorbate. The Freundlich adsorption isotherm for the heterogeneous system is expressed by [18]

$$\log \frac{x}{m} = \log K + \frac{1}{n}(\log C_e) \qquad (1)$$

Where C$_e$ is the equilibrium concentration (mg L^{-1}) and x/m is the amount adsorbed per unit weight of adsorbent (mg g^{-1}). Freundlich constants K, n were evaluated from linear plot of log(x/m) versus log C$_e$. K value was found to be 127.19 (mg g^{-1}), 32.9 (mg g^{-1}) for BTMC and CAC. It is evident from the Table 3 that n value lie between 1 to 10 in BTMC and CAC. This show the favourable adsorption of Hg (II). The Langmuir equation for homogeneous adsorption surface is given by

$$\frac{C_e}{q_e} = \frac{1}{Q_O} b + \frac{C_e}{Q_O} \qquad (2)$$

Where C$_e$ is the equilibrium concentration (mg g^{-1}), q$_e$ is the amount adsorbed at equilibrium (mg g^{-1}). Langmuir constants Q$_o$ and b were calculated from linear plot of C$_e$/q$_e$ verses C$_e$ and found to be 49.75(mgg^{-1}), 44.44(mg g^{-1}), and 0.3284 (L^{-1}mg),0.0851(L^{-1}mg), for BTMC and CAC. The ratio of Q$_0$ value of BTMC and CAC is found to be 1.11.This shows that BTMC is superior to CAC in the adsorption process.

Langmuir isotherm is used to find the relation between sorbate and sorbent using a dimensionless constant separating factor or equilibrium parameter R$_L$ which is denoted by the equation R$_L$ = 1/ (1+b C$_o$) where b is Langmuir constant and C$_o$ is the initial concentration of metal ion[19].The values are tabulated in Table 3. R$_L$ of both BTMC and CAC lies between 0 to 1 indicating favourable conditions for adsorption of Hg (II) ion.

The Temkin isotherm is used to evaluate the adsorption potential of the adsorbents. Temkin isotherm is given by

$$q_e = A + B \, lnC_e \qquad (3)$$

where q_e is the amount of solute adsorbed at an equilibrium concentration of a metal ion in mg g^{-1} C_e is the equilibrium of the solute in mg g^{-1} A is the Temkin constant related to adsorption capacity in mg g^{-1} and B is the Temkin constant related to the intensity of adsorption in L mg^{-1}. The values of A and B are tabulated in Table 3 [20].

3.8 Adsorption Kinetics

To evaluate the kinetics on adsorption of Hg (II) on the BTMC and CAC pseudo-first order and pseudo-second order models were tested with 3,5,7and 10 ppm of Hg(II). Pseudo first -order equation of Langergren is applicable for the adsorption of a liquid/solid system on the basis of solid capacity. The linear form is generally represented by the equation

$$\log(q_e - q_t) = \log q_e - K_1 \frac{t}{2.303} \qquad (4)$$

where q_e (mg g^{-1}) and q_t (mg g^{-1}) are the amounts of adsorption at equilibrium at time t(min) respectively. k_1 (min^{-1}) is the rate constant of the pseudo-first order reaction .The values of k_1, q_e and R^2 were obtained by plotting log $(q_e - q_t)$ versus t Figure 6(a,b) and values tabulated in Table 4.

The correlation coefficient R^2 for pseudo first- order kinetic model was found to be less for both BTMC and CAC. There is a large variation between the experimental and calculated adsorption capacity values which confirms that adsorption of Hg (II) ion on BTMC and CAC do not follow pseudo- first order kinetic model. The linear form of Pseudo-second order kinetics was given by

$$\frac{t}{q_t} = \frac{1}{k_2} \, q_{e^2} + \frac{t}{q_e} \qquad (5)$$

where q_e is the amount of metal ion adsorbed in equilibrium in mg g^{-1}, q_t is the amount of metal ion adsorbed at time t., k_2 (g mg^{-1}min^{-1}) is the rate constant for the adsorption process [21,22]. From the graph between t/q_t and t, q_e and k_2 can be calculated from the slope and intercept of the plot Figure 7 a,b.

From the values in Table 4, it is evident that for all the four concentration of Hg(II) the calculated q_e value lies close to the experimental q_e value proving that both BTMC and CAC follows pseudo-second-order kinetics. The K_2 value decreases with the initial concentration of Hg (II) ion which may be due to the less competition for the sorption surface sites at a lower concentration. To confirm the applicability of the kinetic model, the percentage relative deviation (P %) was calculated using the equation:

Table 3. Isotherm parameters for Hg (II) removal from aqueous solution.

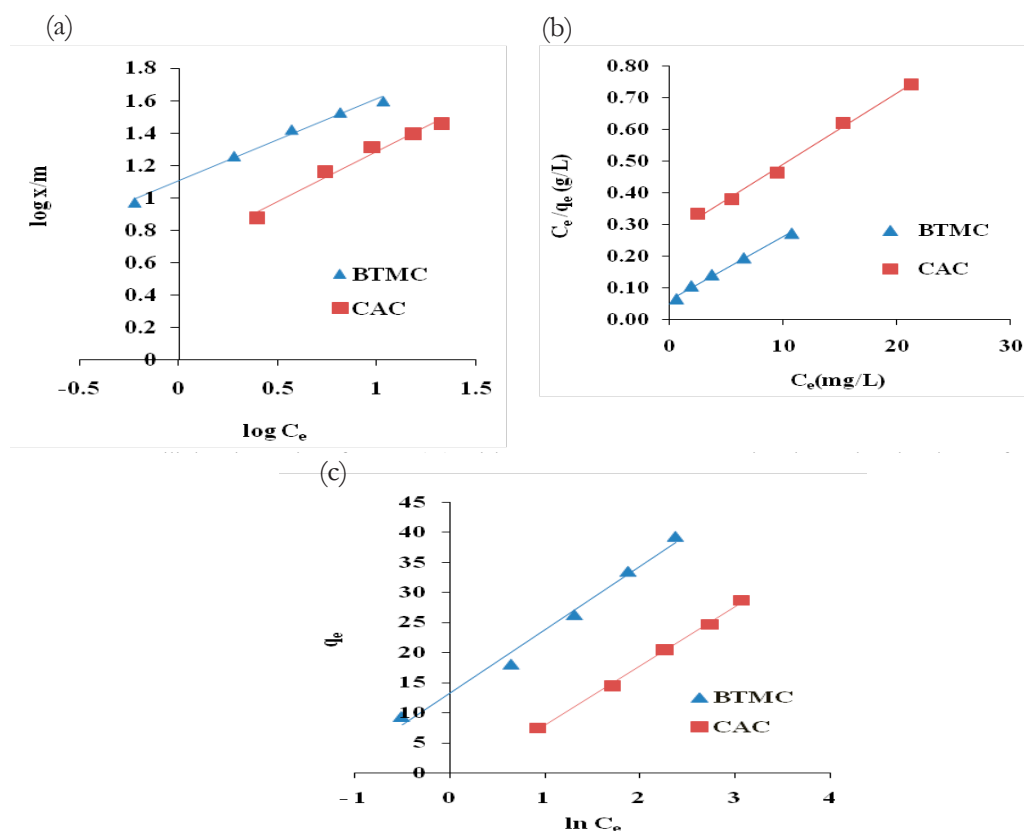| Isotherm model	Parameter	BTMC	CAC
Freundlich	K (mg g^{-1})	127.19	32.9
	n (L^{-1}mg)	1.98	1.33
	R^2	0.9905	0.9373
	Q_0 (mg g^{-1})	49.75	44.44
Langmuir	b (L^{-1}mg)	0.3284	0.0851
	R^2	0.9937	0.9951
	R_L	0.06-0.23	0.19-0.54
Temkin	A	10.54	9.86
	B	13.35	1.83
	R^2	0.9860	0.9978

(a)

(b)

(c)

Figure 5. (a) Freundlich adsorption for Hg (II) with BTMC and CAC.; (b) Langmuir adsorption isotherm for Hg (II) with BTMC and CAC.; (c) Temkin adsorption isotherm for Hg (II) with BTMC and CAC.
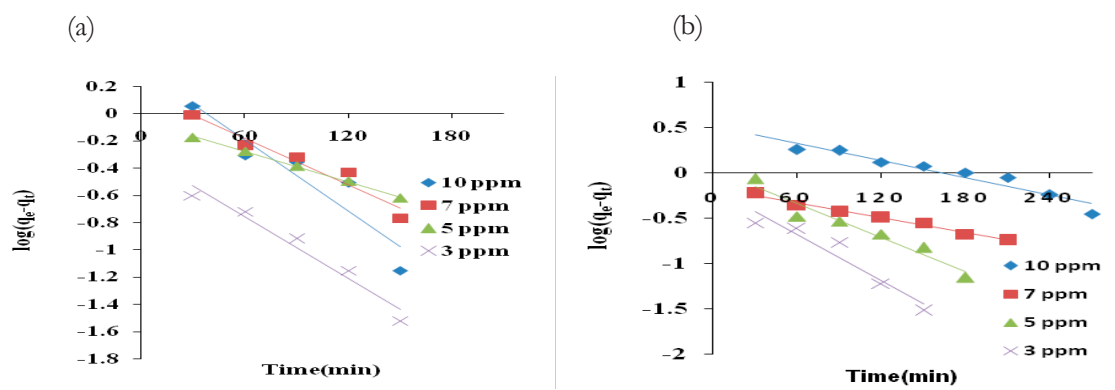
(a)

(b)

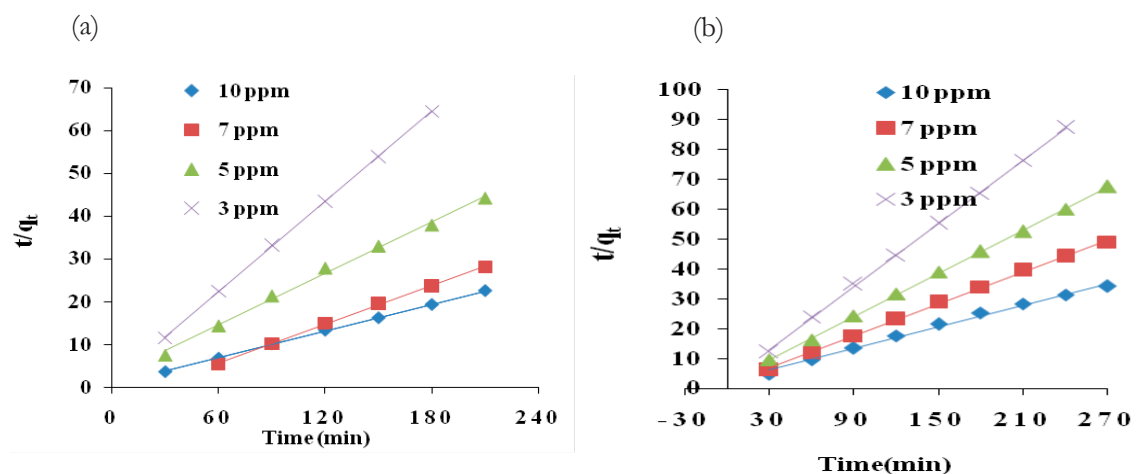**Figure 6.** Pseudo -first- order kinetic fit of Hg (II) on BTMC (a) and CAC (b).

$$P\% = \frac{100}{N} X \left[\frac{q_{e(\exp)} - q_{e(\text{cal})}}{q_{e(\exp)}} \right] \qquad (6)$$

Where $q_{e\,(\exp)}$ and $q_{e\,(\text{cal})}$ are the experimental and calculated value of Hg (II) adsorbed on the adsorbents, N is the number of measurements made. It is found that the lower value of percentage deviation (P %), better is the fit. It is noted that

Table 4. Pseudo- First -Order and Pseudo -Second -Order constants for Hg (II) adsorption on BTMC and CAC at different initial concentration.

Carbon	Con	q_{exp} (mg^{-1}g)	q_{cal} (mg^{-1}g)	K_1 (g mg^{-1} min^{-1})	P%	R^2	q_{cal} (mg^{-1}g)	K_2 (g mg^{-1} min^{-1})	P%	R^2
		Pseudo first order					Pseudo second order			
BTMC	10	9.35	2.13	0.0087	77.21	0.875	9.61	0.018	2.67	1.000
	7	6.50	1.45	0.0057	77.69	0.942	6.62	0.007	1.85	0.999
	5	4.75	1.14	0.0037	76	0.999	4.93	0.020	3.62	0.998
	3	2.80	2.00	0.0076	28.57	0.961	2.87	0.067	2.28	1.000
CAC	10	8.00	3.27	0.0032	59.13	0.922	8.38	0.005	4.48	0.994
	7	5.50	1.47	0.0028	73.27	0.988	5.60	0.023	1.83	0.999
	5	4.00	1.09	0.0063	72.75	0.941	4.15	0.024	3.68	1.000
	3	2.75	1.4	0.0085	49.09	0.922	2.83	0.055	2.84	1.000

(a)   (b)

Figure 7. Pseudo -second -order kinetic fit of Hg(II) on BTMC (a) and on CAC (b).

when P (%) value is less than 5, the fit is considered to be excellent [23].

All kinetic parameters, correlation coefficients and P (%) are listed in Table 4. The correlation coefficient (R^2) for the pseudo-second-order model is much closer to unity. The calculated q_e value is found to be much closer to the experimental q_e value. The percent relative deviation (P %) is also found to be less than 5% in the case of pseudo-second-order kinetics. These results confirm that the adsorption kinetics of Hg (II) ions onto the BTMC and CAC is mainly governed by the pseudo-second-order equation. Similar

kinetic results were observed in the sorption of Hg(II) by other adsorbents like corn starch[24] and ricestraw[25].

3.9 Removal of Hg (II) from Synthetic Waste Water

The applicability of sorbent was tested by performing batch mode studies. The effect of adsorbent dosage on the removal of Hg (II) from synthetic wastewater was analyzed. Figure 8 shows the effect of adsorbent dosage on removal of Hg (II) from wastewater. A minimum dosage of 200 mg BTMC and 310 mg of CAC is essential
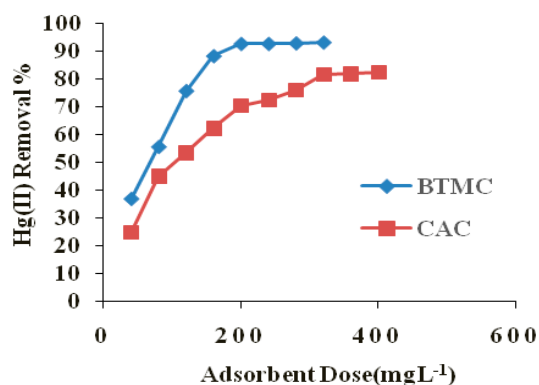
Figure 8. Effects of the adsorbent dose on the removal Hg (II) ions from synthetic wastewater.

for the maximum removal of 93% and 82% of Hg (II) ions from synthetic water. Hence BTMC is found to be efficient in remove mercury from wastewater due to its moderate ion exchange property.

4. CONCLUSIONS

Chemically modified Mangosteen shell using sulphuric acid (BTMC) can serve as an economical and efficient adsorbent for the removal of Hg (II) from aqueous solution. Removal of mercury occurs at optimal contact time of 120 min at pH 5 and carbon dosage of 120 mg for BTMC. The equilibrium data fitted well with Langmuir adsorption studies for BTMC and CAC. The adsorption capacity (Q_0) of BTMC was found to be 49.75mgg^{-1} and 44.44mgg^{-1} for CAC. The pseudo second -order kinetics fits well for BTMC and CAC. The batch study with synthetic wastewater confirms the efficient use of adsorbent in the removal of Hg (II) ions from aqueous solution.

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