BICARBONATE TREATED MANGOSTEEN SHELL CARBON IN REMOVAL OF Ni (II) FROM AQUEOUS SOLUTION-ISOTHERM AND KINETIC STUDIES

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The adsorption of heavy metal Ni (II) from aqueous solution using bicarbonate treated mangosteen shell was studied. The effects of adsorbent dose, contact time, pH, on the removal efficiency of Ni (II) were evaluated by batch mode studies. Adsorption isotherm was studied using Langmuir, Freundlich and Temkin isotherm models. The pseudo-second order kinetic model fits well for the experimental data. The surface morphology and functional groups were analyzed using SEM, EDX, XRD and FT-IR data. All the parameters were compared with CAC. The recovery of the Ni (II) from BTMC is found to be good using 0.1 M HCl.

1. Introduction

Heavy metal pollution in water is of major concern in developing countries as they bio accumulate in food chain and causes adverse effects to environment. Nickel is one of the toxic heavy metal which pollutes the water and threatens human health. [1, 2]. Ni compounds and Ni alloys are used in many industrial and commercial applications. Most Ni is used for the production of stainless steel, non-ferrous alloys and Ni-based super alloys with high corrosion and temperature resistance properties [3].When nickel enters into the human, it penetrates into all organs and accumulates in various tissues and causes tissue damage, which may cause neurotoxicity, hepatotoxicity, nephrotoxicity, gene toxicity, reproductive toxicity, and increase the risk of cancer [4]. Hence there is a need to treat industrial effluents polluted with Ni^{2+} ions before their discharge into the receiving water bodies. The US EPA has set specific nickel limits for wastewater effluent which is 2 mgL^{-1} for short-term effluent reuse and 0.2 mg L^{-1} for long-term effluent reuse [5]. Utilization of agro-wastes as adsorbent is currently receiving wide attention because of their abundant availability and low-cost owing to relatively high fixed carbon content and presence of porous structure [6].

Activated carbon derived from various agricultural waste products, such as almond husks [7], peanut shells [8], Lansium domesticum peel [9] are used in nickel removal. The main objective of this work is to modify mangosteen shell using sulphuric acid and sodium bicarbonate and analyze it for its efficiency to remove nickel from aqueous solution. Commercial activated carbon procured from the Merk India was used for comparative studies**.**

2. Materials and methods

2.1. Preparation of adsorbent

Mangosteen shell which was collected from Thenkasi, India was washed with distilled water, dried to 110^0C powdered and sieved using 20-50 ASTM mesh. The material was treated with con H_2SO_4 (1:1) weight ratio and kept in a hot air oven at 150 ± 5^0C for 24 h. The carbonized

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material obtained 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 adsorbent obtained was again washed with distilled water, dried and sieved to 20-50 ASTM mesh size and labeled as Bicarbonate Treated Mangosteen Shell carbon (BTMC).

The Commercial Activated Carbon (CAC) procured from Merk India was broken and sieved to 20-50 ASTM mesh size.

2.2 SEM-EDX, XRD and FTIR study

The surface morphology of adsorbent was found based on scanning electron microscope. Energy dispersive X-ray analysis helps to confirm the elements present in the adsorbent before and after adsorption of the metal ions. X-ray diffraction studies helps to confirm the nature of the adsorbent. Fourier transform infrared spectroscopy helps in identifying the functional groups present on the surface of the adsorbent in 400-4000 cm^{-1}.

2.3 Batch adsorption experiments

Adsorption studies were carried out by varying contact time (30-210 min), solution pH (1-10), adsorbent dosage (40- 280 mg).For each study required quantity of adsorbent dose was added to 100 mL of 10 mg/L-50 mg/L of Ni (II) solutions taken in a polythene containers agitated in a mechanical shaker. The carbon was separated by filtration and the filtrate were analyzed by spectrophotometer for Ni(II) content at 470 nm using DMG(Dimethyl Glyoxime)[10].Adsorption isotherm studies were carried out with different initial concentrations of Ni(II) while maintaining the carbon dosage at constant level. Each experimental procedure were repeated thrice and the average result is presented in this paper.

3. Results and discussion

3.1Carbon characteristics

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

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

3.2. Fourier transform infrared spectroscopy analysis

FTIR spectrum of BTMC before and after adsorption of Ni (II) is shown in Fig 1 (a, b) The shift in absorption peaks are tabulated in Table 2.It is evident that some of the peaks shift or disappear indicating the incorporation of heavy metal ion Ni (II) within the adsorbent through the interaction of the active functional group after adsorption.

Table 2. FTIR spectral data of different functional groups on or before adsorption of Ni(II) on BTMC.

Frequencies(cm^{-1})		
Before Adsorption	After Adsorption	Corresponding functional groups
3425	3394	-OH stretching vibration
2981	Disappear	C-H stretching
2372	2380	C≡ C stretching
1427	1404	Sulphonic acid
1222	1219	-CO stretching vibration of ether
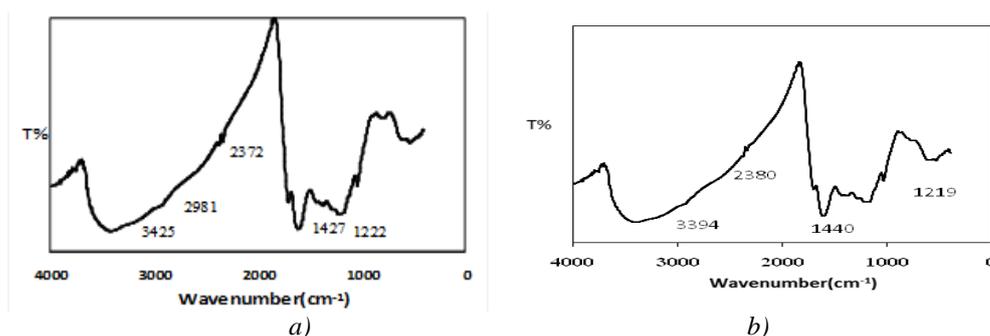
Fig. 1. (a ,b) FT-IR spectra of BTMC before and after adsorption of Ni (II).

3.3. SEM-EDX Analysis

The SEM image of the adsorbent BTMC before and after adsorption of Ni (II) were shown inFig. 2(a,b) respectively. 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 Ni (II) ion after adsorption. The EDX analysis of BTMC shows Ni (II) ion peaks in addition to other peaks confirming the adsorption of metal on the adsorbent surface Fig. 2(c,d)
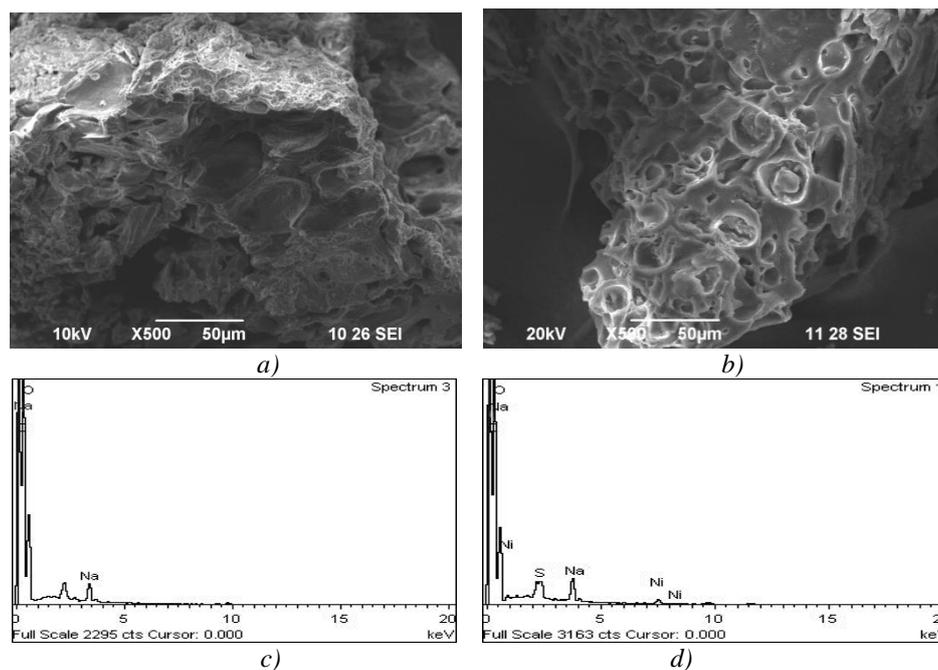
Fig. 2 (a) SEM image of BTMC before adsorption. (b) SEM image of BTMC after adsorption; c) EDX image of BTMC before adsorption, d) EDX image of BTMC after adsorption.

3.4.X Ray Diffraction Studies

The X- ray diffraction (XRD) pattern of BTMC (Fig 3a, b) shows amorphous nature due to the presence of cellulosic material as explained by Reddy et al [11]. X-ray diffractogram of Ni (II) adsorbed BTMC shows shift in peaks which may be due to the binding of nickel on BTMC.
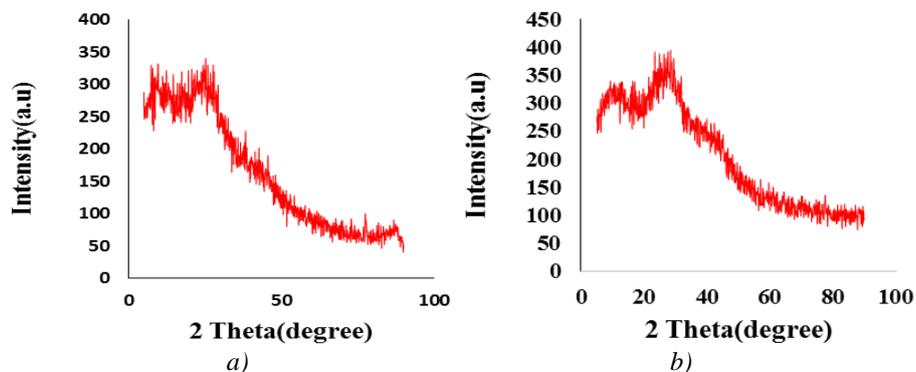
Fig.3. XRD image of
a) BTMC before Ni(II) adsorption; b) BTMC after Ni(II) adsorption.

3.5. Effect of contact time

Equilibrium time is an important parameter to know about adsorption process. The Fig. 5 shows the effect of contact time on the adsorption of Ni (II) on BTMC and CAC .The results show that the removal of nickel ion increases with time and attains equilibrium in 30 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 diffuse into the intra particle pore of the adsorbent.
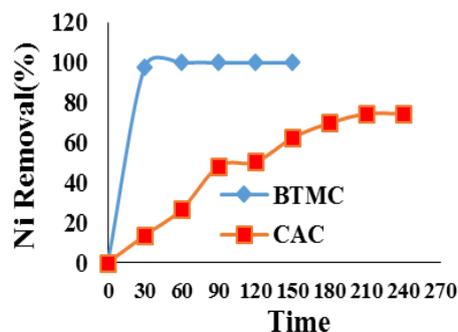
Fig. 5. Effect of contact time on the removal of Ni (II) by BTMC and CAC.

3.6. Effect of pH

The removal of metal ion from aqueous solution by adsorption is highly dependent on the p^H of the solution. Fig. **6** show the effect of pH on the removal of Ni (II) by BTMC and CAC. It was observed that maximum removal of 99 % was observed for BTMC at pH 5 and 84 % at pH 8 for CAC.
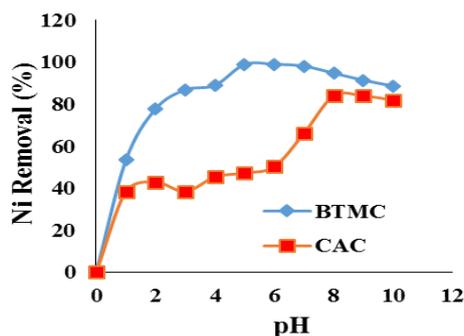
*Fig. 6. Effect of pH on the removal of Ni (II) by BTMC and CAC at
(Carbon Dose =100 mg/100 mL).*

3.7. Effect of adsorbent dose

The effect of adsorbent dosage on the percentage removal of Ni (II) is shown in Fig 7. It was observed that initially the percentage removal increases sharply with increase in adsorbent dose but after 60 mg dose of BTMC and 240 mg dose of CAC the percentage removal value is constant due to reduction in concentration gradient. The maximum removal efficiency of Ni (II) for BTMC and CAC are 99 % and 88 % respectively. The increase in removal efficiency of Ni (II) ion may be due to the increase in adsorbent mass or availability of large number of exchangeable sites for adsorption.
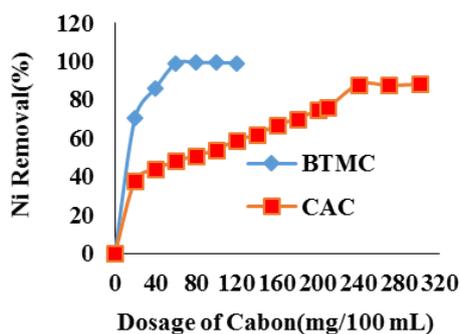
*Fig. 7. Effect of carbon dosage on the removal of Ni (II) by BTMC
and CAC at (pH =5,8).*

3.8. Isotherms study

The adsorption isotherms are important parameters used to understand the mechanism of adsorption. Langmuir, Freundlich, and Temkin isotherm were used to study adsorption process and constant parameters were calculated. The Freundlich, Langmuir and Temkin isotherm were expressed by following equation:

$$\log x/m = \log K + 1/n (\log C_e) \tag{1}$$

where C_e is the equilibrium concentration (mg L^{-1}) and x/m is the amount adsorbed per unit weight of adsorbent (mgg^{-1}) and Freundlich constants K, n can be obtained from the graph between $\log(x/m)$ versus $\log C_e$[12]

$$C_e/q_e = 1/Q_o b + C_e/Q_o \tag{2}$$

where C_e is the equilibrium concentration (mg g^{-1}), q_e is the amount adsorbed at equilibrium (mg g^{-1}) and Q_o and b are Langmuir constants related to adsorption capacity and energy of adsorption respectively [13].

$$q_e = A + B \ln C_e \tag{3}$$

where q_e is the amount of solute adsorbed at equilibrium concentration of 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 intensity of adsorption in L mg^{-1}[14]

  The value of n and correlation coefficient (R^2) predict that the adsorption isotherm is favorable and feasible. The value of $1/n < 1$ shows the favorability and feasibility in intercept and R^2.The high correlation coefficient (R^2) shows the most favorable result for the adsorption of Ni (II) on BTMC by Langmuir model.

Langmuir, Freundlich and Temkin plots were shown in Fig. 8(a,b.c) and the values obtained are given in the Table 3.
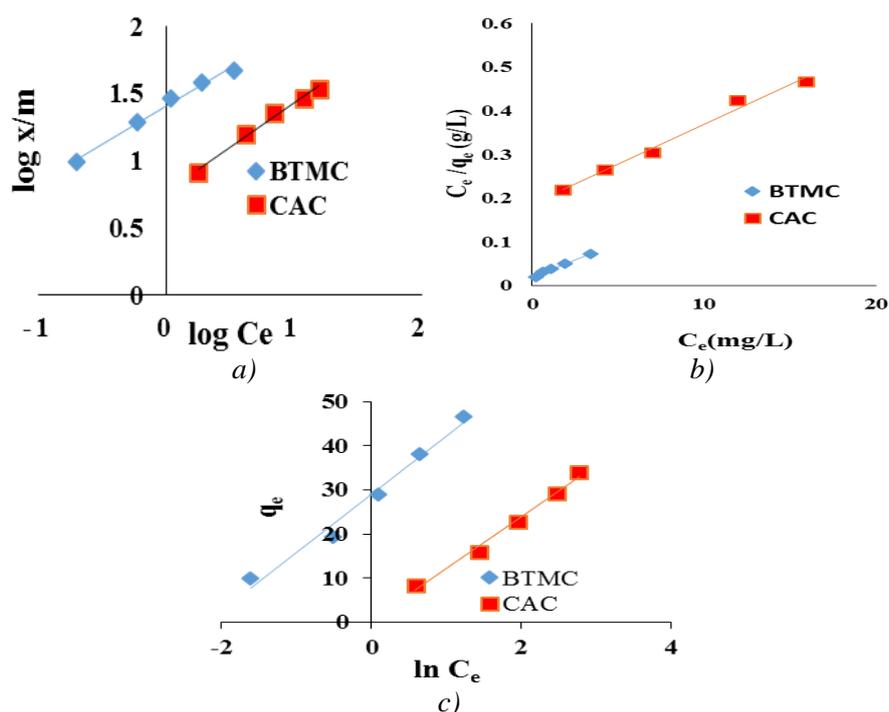
Fig. 8 Adsorption isotherm for Ni (II) with BTMC and CAC
(a) Freundlich adsorption isotherm. (b) Langmuir adsorption isotherm
. (c) Temkin adsorption isotherm

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

Isotherm model	Parameter	BTMC	CAC
Freundlich	K(mg g^{-1})	254.3	59.33
	n (L^{-1}mg)	1.78	1.54
	R^2	0.989	0.987
	Q_0(mg g^{-1})	57.14	54.94
Langmuir	b (L^{-1}mg)	0.093	0.1
	R^2	0.999	0.986
	R_L	0.17-0.51	0.16- 0.5
Temkin	A	13.24	11.83
	B	28.98	0.23
	R^2	0.980	0.989

3.9 Kinetics study

To study about the mass transfer and chemical reactions, pseudo 1st order, pseudo 2nd order and intra-particle diffusion models were used to determine the experimental data. The linear rate equation of pseudo 1st order equation is given as[15]

$$\log (q_e - q_t) = \log q_e - K_1/2.303t \tag{4}$$

where q_e (mg g^{-1}) and q_t (mg g^{-1}) are the amount of adsorption at equilibrium and at time t(min) respectively. k_1 (g mg^{-1}min^{-1}) is the rate constant of the pseudo-first order reaction and R^2 of Ni (II) at different concentration were noted from the linear plot of $\log(q_e - q_t)$ vs t as shown in Fig. 9(a,b) and tabulated in Table 4.

Pseudo -second order kinetics were analyzed using the linear equation.

$$t / q_t = 1 / k_2 q_e^2 + t / q_e \tag{5}$$

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. [16,17].The k_2, q_e and regression coefficient value (R^2) under different concentration were calculated from the linear plot of t/q_t vs t as shown in Fig. 10(a,b)

The results were compared with the correlation coefficients (R^2) value and shown in Table 4. The regression coefficient values for second order rate equation is high when compared to pseudo 1st order kinetics. $q_{e(exp)}$ values of second order agreed well with $q_{e(cal)}$ value as compared to pseudo 1st order. The k_2 value decreases as the Ni (II) ion concentration increases since at low concentration there is less competition for sorption sites. To confirm the applicability of kinetic model fitting to data, the percentage relative deviation (P %) was calculated using the equation:

$$P\% = 1/N \times 100 \ (q_{e \ (exp)} - q_{e(cal)}/q_{e(cal)}) \tag{6}$$

where $q_{e \ (exp)}$ and $q_{e \ (cal)}$ are the experimental and calculated value of Ni (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 when P (%) value is less than 5, the fit is considered to be excellent [18].

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. These results confirm that the adsorption kinetics of Ni (II) ions onto the BTMC and CAC is mainly governed by pseudo-second-order equation. This means that the overall rate of Ni (II) ion adsorption process may be controlled by the chemical process. A similar phenomenon was also observed for Ni (II) on other natural adsorbent. Hence, it may be concluded that adsorption follows second- order Kinetics. The C, K_{id} and R^2 value were calculated from the plot of q_t vs $t_{1/2}$ and reported in Table 5.
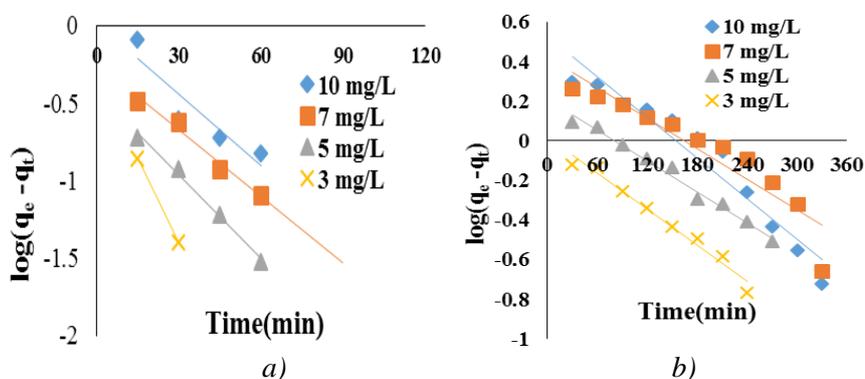
Fig. 9. (a,b) Pseudo- first order kinetic fit of Ni (II) on BTMC and CAC.
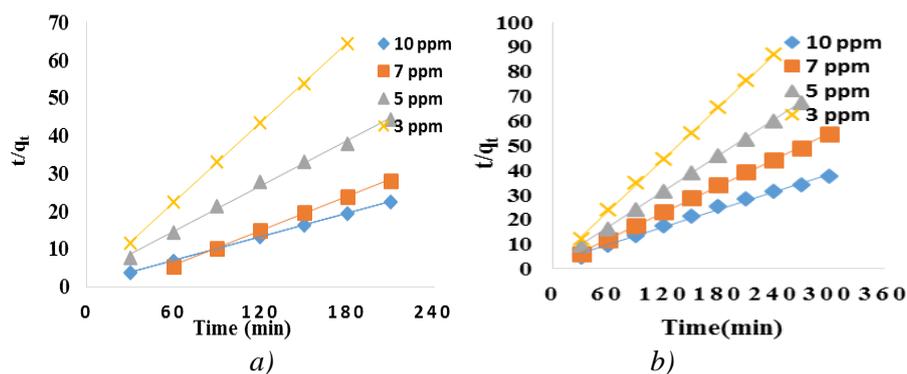
Fig. 10. (a, b) Pseudo s-econd order kinetic fit of Ni (II) on BTMC and CAC.

Table 4. Pseudo first -order and pseudo second -order constants for Ni (II) adsorption on BTMC and CAC at different initial concentration.

Carbon	Con(mg L^{-1})	q_{exp} (mgg^{-1})	q_{cal} (mgg^{-1})	K_1 (g mg^{-1} min^{-1})	P%	R^2	q_{cal} (mgg^{-1})	K_2 (gmg^{-1}min^{-1})	P%	R^2
				Pseudo- first order				**Pseudo- second order**		
BTMC	10	9.97	1.05	0.0154	89.52	0.8466	10.13	0.0640	1.60	0.999
	7	7.00	1.75	0.0143	75.01	0.9809	7.07	0.1116	1.02	0.9991
	5	4.99	2.63	0.018	47.29	0.9916	5.04	0.2138	1.05	1
	3	2.99	2.04	0.0363	31.77	1	3.04	0.3433	1.75	1
CAC	10	7.80	3.36	0.0034	56.94	0.9367	8.18	0.0044	4.61	0.994
	7	5.20	2.66	0.0026	48.90	0.8801	5.44	0.0043	4.37	0.982
	5	3.70	1.61	0.0026	56.41	0.9848	3.89	0.0073	4.91	0.99
	3	2.35	1.04	0.003	55.74	0.9752	2.47	0.0128	4.97	0.991

3.10. Adsorption mechanism

The steps involved in adsorption process are [19]

- The movement of adsorbate molecules from the bulk to external surface of the adsorbent (Film diffusion).
- The adsorbate move to the interior surface of the adsorbent particle (Intra particle diffusion).
- Sorption of the solute on the interior surface of the pores and capillary spaces of the adsorbent (Sorption).

3.11. Weber- Morris intra- particle diffusion model

The kinetic data fit well to chemisorption model, to verify the influence of mass transfer resistance on the binding of Ni (II) to the adsorbent and to confirm diffusion mechanism Weber and Morris intra- particle diffusion model was given by

$$q_t = k_{id}\, t^{1/2} \tag{7}$$

where q_t is the amount adsorbed per unit mass of adsorbent (mg g^{-1}) at time t (min) and K_{id} the intra- particle diffusion rate constant (mg g^{-1} min$^{-1/2}$). If the intra- particle diffusion is involved in the adsorption process, then a plot of the amount of Ni (II) adsorbed per unit mass of adsorbent (q_t) against square root of time ($t^{1/2}$) will give a straight line and the particle diffusion would be the rate controlling step if this line pass through the origin. However in BTMC and CAC the plots were not linear and do not pass through the origin. The plot shows that intra particle diffusion was not the only rate limiting step but also rate controlling step for adsorption or both process may operate simultaneously. Fig 11(a,b)
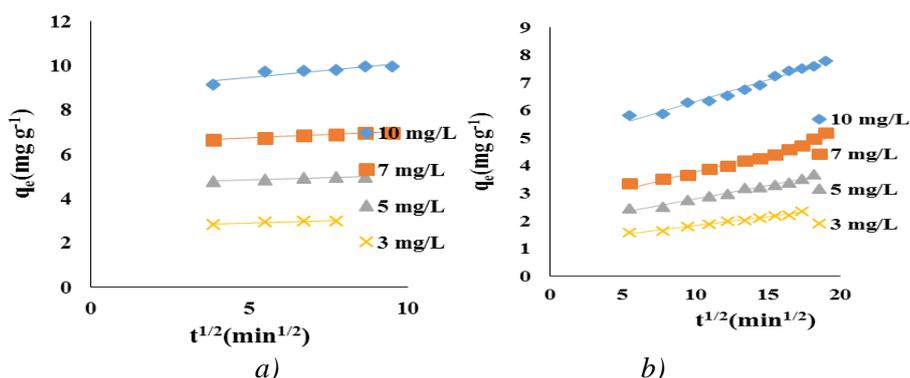
Fig. 11. (a,b) Intra- particular diffusion plot for the adsorption of Ni (II) on BTMC and CAC.

3.12. Boyd's kinetic model

The Boyd's kinetic plot helps to find the rate determining step involved in adsorption process. The Boyd's kinetic equation [20] is given by

$$F=1-6/\pi^2 \exp (B_t) \qquad (8)$$

where $F = q_e/q_t$ F represents the amount of Ni (II) adsorbed at time t. B_t is the mathematical function of F.

Eq (8) can be rearranged to

$$B_t = -0.4977 – \ln (1-F) \qquad (9)$$

The plot of B_t versus t can be used to test the linearity of experimental values. If the plots are linear and pass through the origin the slowest step in the adsorption process may be internal diffusion. From Fig 12 (a,b). It was noted that the plots are linear but do not pass through the origin predicting that the adsorption process may be controlled by film diffusion.
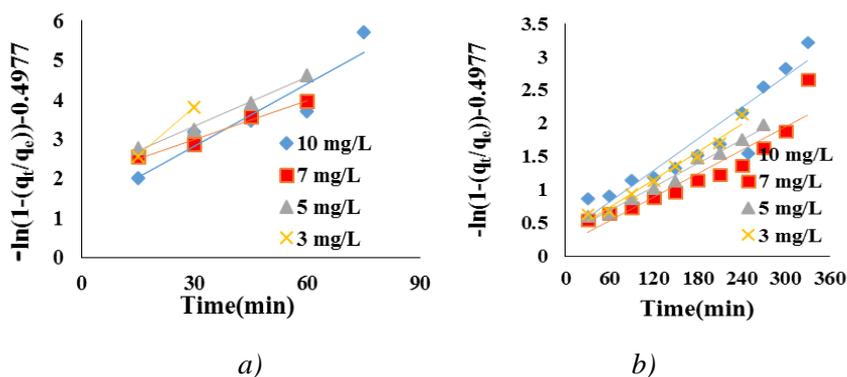
Fig. 12. (a,b) Boyds kinetic plot for adsorption of Ni (II) ion on BTMC and CAC.

3.13. Film and pore diffusion coefficient

To confirm the nature of diffusion process, assuming the spherical geometry for the sorbents, film and pore diffusion co-efficient is calculated using the expression

$$D_{p=} 0.03 \; r_0^2/ \; t^{1/2} \qquad (10)$$

$$D_f = 0.23 \; r_0 \; c* \; /ct^{1/2} \qquad (11)$$

where, r_0 is the radius of the sorbent expressed in cm^2, D_p the pore diffusion coefficient expressed in $cm^2\ sec^{-1}$, D_f the film diffusion co- efficient expressed in $cm^2\ sec^{-1}$ $c*$ /c is equilibrium loading factor of the sorbent and $t^{1/2}$ is half-life period expressed in seconds. For the adsorption of heavy metals on carbon surface Michaelson et al proposed film diffusion to be the rate determining process, if the value of film diffusion co-efficient (D_f) is between $10^{-6} – 10^{-8}\ cm^2\ sec^{-1}$. If the pore diffusion were to be the rate- limiting factor, the pore diffusion co-efficient (D_p) should be in the range of $10^{-11} – 10^{-13}\ cm^2\ sec^{-1}$[21]. The results for BTMC and CAC is presented in Table 5 shows that removal of Ni (II) follows film diffusion as the coefficient values are closer to $10^{-6} – 10^{-8}\ cm^2\ sec^{-1}$.

Table 5. Intraparticular, film, pore diffusion coefficient of BTMC and CAC at different concentrations.

Carbon	Concentration	Intra particular Diffusion Coefficient Kid ($mg\ g^{-1}min^{-1/2}$)	Film Diffusion Coefficient D_f ($cm^2\ sec^{-1}$)	Pore Diffusion Coefficient, D_p ($cm^2\ sec^{-1}$)
	10	0.129	1.28×10^{-7}	6.19×10^{-8}
	7	0.063	7.96×10^{-8}	$5.75 \times 1\ 0^{-8}$
BTMC	5	0.040	6.32×10^{-8}	6.4×10^{-8}
	3	0.037	3.52×10^{-8}	5.63×10^{-8}
	10	0.158	1.25×10^{-7}	4.69×10^{-8}
CAC	7	0.132	6.58×10^{-8}	3.53×10^{-8}
	5	0.097	4.71×10^{-8}	3.54×10^{-8}
	3	0.064	3.89×10^{-8}	4.87×10^{-8}

3.14. Removal of Ni (II) from synthetic wastewater

The applicability of sorbent was tested by performing batch mode studies. The effect of adsorbent dosage on the removal of Ni (II) from synthetic wastewater was analysed. Fig 13 shows the effect of adsorbent dosage on removal of Ni (II) from wastewater. A minimum dosage of 120 mg BTMC and 360 mg of CAC is essential for the maximum removal of 96 % and 85 % of Ni (II) ions from synthetic wastewater. Hence BTMC can be noted as an efficient adsorbent to remove nickel from wastewater due to its moderate ion exchange property.
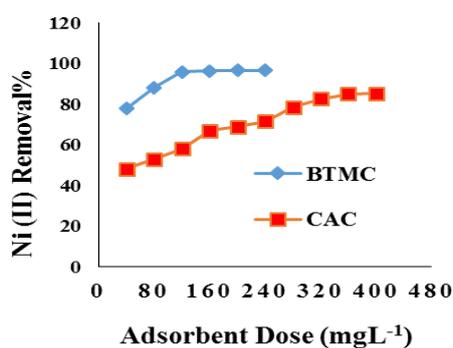
Fig. 13. Effect of the adsorbent dose on the removal Ni (II) ions from synthetic wastewater (Con: 10 mg L^{-1}, pH: 5.0,8.0 and contact time: 3&5 h for BTMC &CAC).

3.15. Desorption and regeneration studies

In order to find out the regeneration capacity of carbon 0.1 N HCl was used for regenerating BTMC and 0.5 N HCl for CAC for five cycles of operation. Fig 14(a,b) shows the adsorption-desorption percentage of BTMC and CAC. The results shows slight decrease in the sorption of Ni (II) ions from 95% to 85% when treated with BTMC giving better recovery of

Ni (II) ions. The decrease in the sorption may be due to the opening of more surface active sites present on the sorbent surface on repeated regeneration cycles.

However the recovery of Ni (II) ions decreased rapidly from 65 % to 48 % in case of CAC in fifth cycle. It was observed that BTMC has a potential for repeated use and recovery of Ni (II) ions.
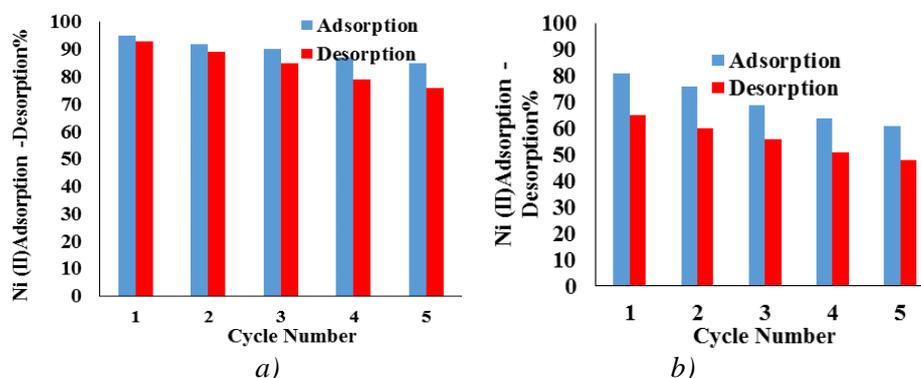
Fig. 14. a) Desorption and b)regeneration study of BTMC and CAC.

4. Conclusions

An economically efficient adsorbent was prepared from Mangosteen shell using sulphuric acid and sodium bicarbonate as modifiers to remove Ni (II) from aqueous solution.. The manufacturing process is simple hence it can be used as an alternative for high cost adsorbents. The mechanism of adsorption may be ion -exchange process. The adsorption capacity (Q_O) of BTMC was found to be $57.14 mgg^{-1}$ and 54.94 mgg^{-1} for CAC. The pseudo -second order kinetics fits well showing that BTMC may follow chemisorption process. The Boyd's kinetic model predicts the actual rate determining step involved in the adsorption process. The efficiency of Ni (II) removal is tested using synthetic wastewater and desorption studies show good regeneration capacity of BTMC.

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