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# CHARACTERIZATION THE CATION EXCHANGERS BASED ON MICROCRYSTALLIN CELLULOSE AND ITS APPLICATION

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## Summary:

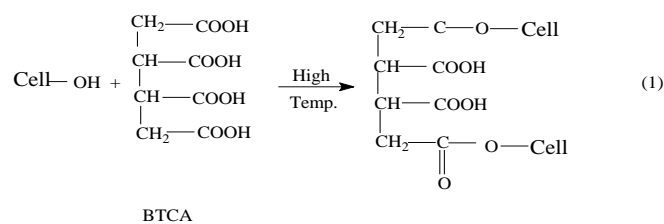
Cation exchanger was prepared via reaction of microcrystalline cellulose with butane tetra carboxylic acid at elevated temperature. Factors affecting reaction were studied. These factors were acid concentration, reaction time and temperature. The cation exchanger sample were characterized by FT-IR spectroscopy and by estimating the carboxyl content expressed as meq.-COOH/100 g sample as well as estimation of solubility percent in distilled water. The so-obtained cation exchanger sample were utilized for the removal of Pb (II) from aqueous solutions. Adsorption studies have been carried out to determine the effect of agitation time, pH, adsorbent concentration and adsorbate concentration on the adsorption capacity of Pb (II) ions. Langmuir and Freundlich models were applied in the adsorption studies. The study showed that the cation exchanger sample were effectively used in adsorption of Pb (II) from aqueous solutions. Kinetic parameters were also evaluated .The adsorption data follows second order kinetics and obeyed the Langmuir and Freundlich isotherms. The promising results obtained in this paper encourage us to use modified this materials in waste water treatment as low cost adsorbent instead of high expensive activated carbon.

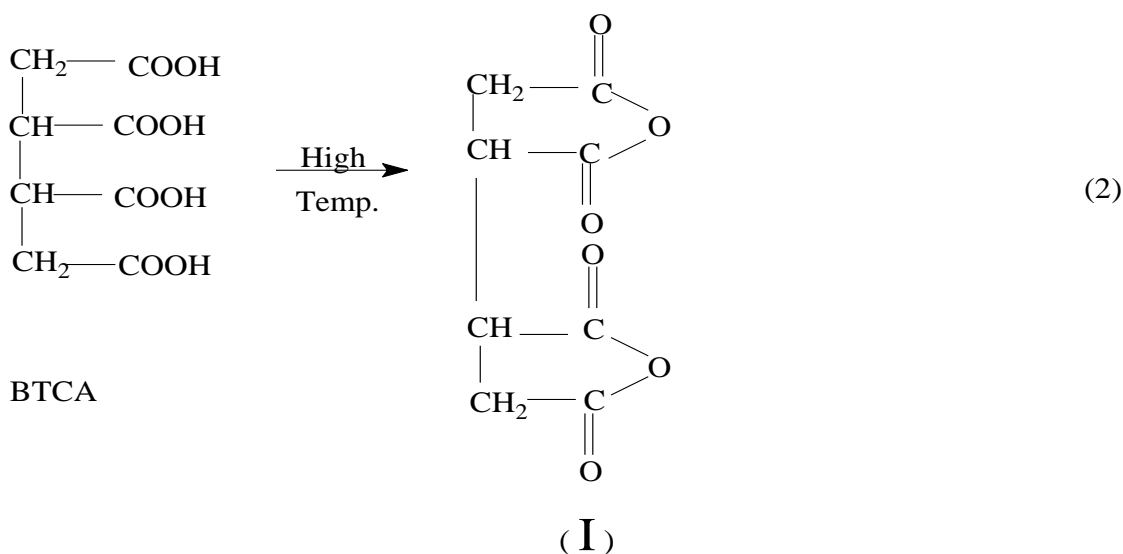
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## 1. INTRODUCTION

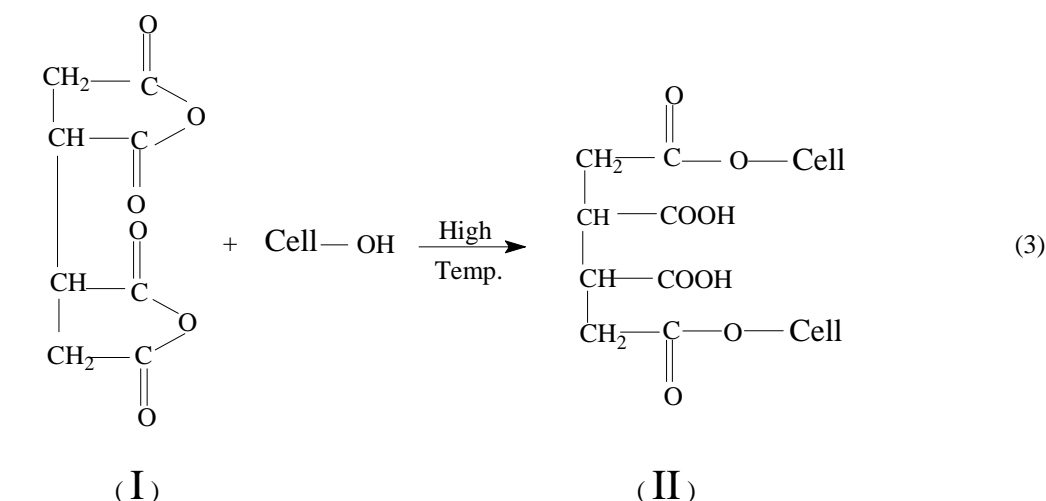
Microcrystalline cellulose (MCC) reacts with butane tetra carboxylic acid and gives cation exchanger when it is subjected to high temperature. In this study, the presence of butane tetra carboxylic acid at high temperature would allow to form butane tetra carboxylic acid anhydride, BTCAA. MCC along with (BTCAA), during heating would allow the anhydride to react with the cellulose hydroxyls of MCC to form cation exchanger as shown below in Eq. 1 - 3.

Hashem A. <sup>(1)</sup> reported that, the IR spectra are a useful tool for investigating the structure of modified and unmodified microcrystalline cellulose.





dianhydride of BTCA



dianhydride of BTCA

Cation exchanger

## 2. Materials And Methods

### 2.1. Materials

Butane tetra carboxylic acid (BTCA), Microcrystalline cellulose (MCC) particle size 2-20µm, surface area 15000cm<sup>2</sup>/g, lead acetate, cadmium acetate, mercuric acetate, , zinc acetate, sodium carbonate, acetic acid and ethylene diamine tetra acetic acid (EDTA) were reagent grade chemicals and supplied from BDH product ,England

### 2.2. Methods

#### 2. 2.1. Preparation of cation exchanger

The preparation of cation exchanger as follows: To a beaker containing 5 g microcrystalline cellulose particle size 2-20µm, certain weight of butane tetra carboxylic acid (dissolved in the least amount of distilled water) was added under continuous mixing with a spatula until a

homogenous paste was obtained. The paste was then transferred to a Pyrex petridish and dried at 140 °C for 2h in an air -circulated oven. The thermally treated sample was then cooled to room temperature and then ground. Soluble by-products and unreacted butan tetra carboxylic acid was washed several times with water:ethanol mixture (20:80) for 2h, and finally the purified material dried at 60 °C for 2h.

**2.2.2. Adsorption studies**

All the adsorption experiments were carried out by the following procedure: about 0.05 g of the adsorbent was shaken with 100 ml metal solution of varying concentration in different Erlenmeyer flasks. Initial pH of the solution was adjusted using 0.05M solution of acetic acid and Na<sub>2</sub>CO<sub>3</sub>. The contents were continuously agitated in a thermo-stated shaking water-bath at 30°C. At the end of contact time, the metal ion solutions were separated by filtration. The blank experiments were simultaneously carried out without the adsorbent. The adsorption capacity q<sub>e</sub> and percent removal of Pb (II) by cation exchanger were determined by measuring the concentration of the remaining metal ion on the resulting filtrate by direct titration against standard EDTA solution as follows:

$$q_e (mg / g) = \frac{(C_o - C_t) \cdot V(l)}{W} \quad (4)$$

$$\% \text{ Removal} = \frac{(C_o - C_t)}{C_o} \times 100 \quad (5)$$

**2.3. Analysis**

**2.3.1. Determination of carboxyl content**

The carboxyl content of the cation exchanger was determined according to the reported method <sup>(2)</sup>.

Accurately 0.2 g of of the cation exchanger was introduced in 125 ml of Erlenmeyer flask containing 50 ml of NaOH solution (0.03N). The blank experiment was

carried out without the cation exchanger sample. The flasks were left at room temperature over night. The flasks were titrated with standard HCl using phenolphthalein as indicator. The carboxyl content of the cation exchanger was calculated as follows:

$$\text{Carboxyl content} = \frac{(V_0 - V_1) \times N \times 100}{W} = (6)$$

*m.eq -COOH / 100 g samplel*

Where V<sub>0</sub> is the volume of HCl consumed in blank experiment,

V<sub>1</sub> is the volume of HCl consumed in the cation exchanger sample,

N is the normality of standard HCl,

W is the weight sample (g).

**2.3.2. FT-IR Spectroscopy**

The FT-IR spectra of MCC, MCC treated by BTCA (cation exchanger) were recorded on a Nexus 670 FT-IR spectrometer, (Nicolet, USA) in the spectral range 4000-400 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup> using the KBr disk technique.

**2.3.3. Determination of solubility % of cation exchanger**

This test is very important to be sure that the adsorbent material is completely insoluble in distilled water.

The solubility percent of the cation exchanger were measured according to a reported method <sup>(3)</sup> as follows:

0.5 g of cation exchanger sample was introduced in 100 ml of Erlenmeyer flask containing 50 ml distilled water. The flask was placed in the thermostatic water-bath at 60°C for 2h with continuous shaking. At this end, 30 ml of clear solution was withdrawn and placed in Petri dish of known weight. Dry the Petri dish containing sample in an electric oven at 100°C until constant weight. Weight the Petri dish again and calculate the increase in weight. The solubility % was calculated as follows:

$$\text{Solubility \%} = \frac{\text{Increase in weight} \times 50}{0.5 \times 30} \times 100 \quad (7)$$

The solubility percent of cation exchanger (optimized sample) not more than 10 %

### Results and Discussion3.

The FT-IR spectra of MCC and cation exchanger are illustrated in Fig.1. The difference in fingerprint regions are clear and confirm the esterification process. Fig.1

(a) shows the peaks at  $1643 \text{ cm}^{-1}$  characteristic for the carbonyl groups of MCC. Fig. 1(b) shows the appearance of new peak at  $1839 \text{ cm}^{-1}$  characteristic of carboxylic acid ester due to the formation of cation exchanger after thermal treatment with BTCA. The FT-IR spectra (b) also shows a broadness at  $2900 \text{ cm}^{-1}$  characteristic of  $-\text{OH}$  of carboxylic acid of the obtained ester (cation exchanger

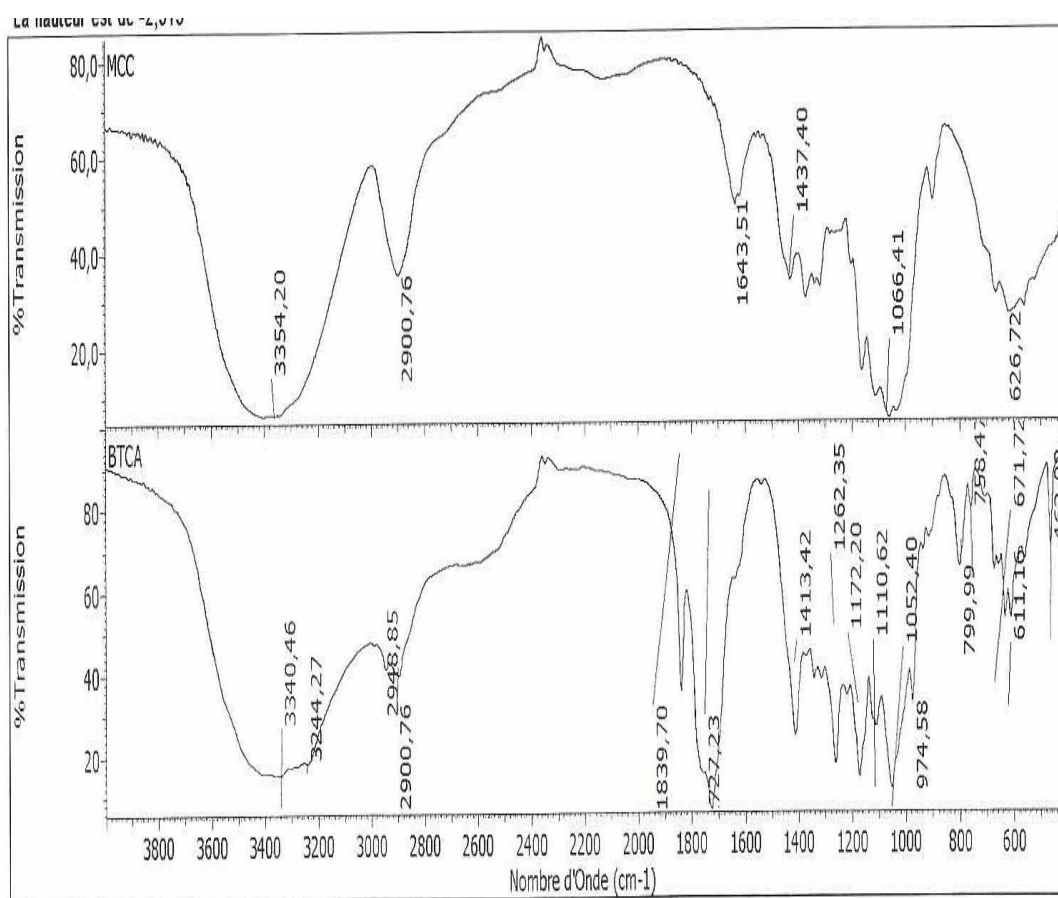


Fig. 1: FT-IR spectra of Mcc (a) and cation exchanger (b).

### 3.1. Effect the type of cations on adsorption capacity

The effect of type of cations on adsorption capacity was investigated using different metal cations such as Hg (II), Pb (II), Cd (II) and Zn (II). Table 1 Shows the adsorption capacity of Hg (II), Pb(II), Cd(II)

and Zn (II). onto cation exchanger at  $30^\circ\text{C}$ . The data indicate that adsorption capacity values depends on the metal cations used. The adsorption capacity for these heavy metal ions follow the following order:

Pb (II) > Hg (II) > Cd (II) > Zn (II)

The differences in adsorption capacity of these metal ions on the adsorbent material could be attributed to the difference in stability constants of the formed complexes

<sup>(4)</sup>. For this reason, the adsorbent material (cation exchanger) was utilized for the removal of Pb (II) ions from aqueous solution in this study.

Table 1: Effect of type of cations on their adsorption capacity onto Cation exchanger at 30 °C

Metal cations used	q <sub>e</sub> (mg/g)
Pb (II)	625.9
Hg (II)	557.6
Cd (II)	229.2
Zn (II)	65.8

Adsorption conditions: Metal cations conc., 400 mg/l; pH, 4.5; agitation time, 2h; adsorption temperature, 30 °C; carboxyl content, 248 m.eq /100 g sample and adsorbent concentration, 0.5(g/l).

### 3.2. Factors affecting preparation of cation exchanger

#### 3.2.1. Effect of Butane tetra carboxylic acid concentration

Table 2 and (Fig.2) shows the dependence of carboxyl content of cation exchanger on BTCA concentration when MCC particles were subjected to esterification at different concentrations of BTCA.

Obviously, the carboxyl content of cation exchanger increases significantly from

133.321 to 244.752 m.eq/100g sample by increasing the concentration of BTCA concentration from 2.13 to 17.1 m.mole/l.

The enhancement in carboxyl content could be interpreted in terms of greater availability of BTCA molecules in the proximity of MCC molecules which were converted to anhydride under the effect of high temperature employed. The formed anhydride will react with cellulose hydroxyls of MCC particles to form cation exchanger as shown in Equation 1 and 3.

Table 2: Effect of BTCA concentration on the extent of modification expressed as m.eq-COOH/ 100 g sample of cation exchanger

BTCA (m.mole/l)	Carboxyl content (m.eq/100 g sample)
2.1367	133.3
4.2735	195.8
6.4102	231.2
8.5470	239.5
17.09402	244.7

Reaction conditions: reaction temperature, 140 °C for 2h.

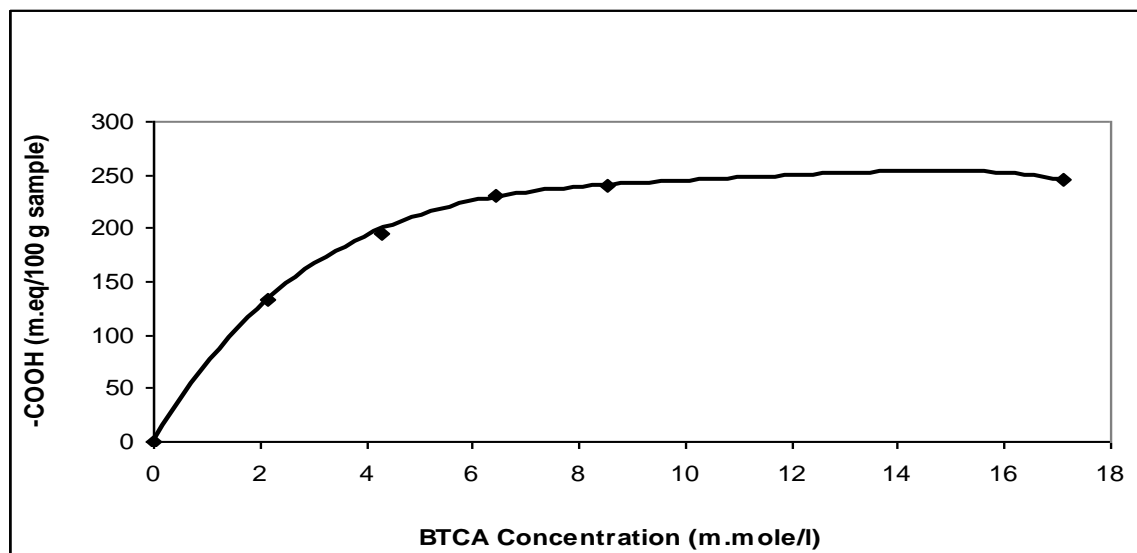


Fig. 2: Effect of BTCA concentration onto extent of MCC modification  
 Reaction Conditions: MCC, 2g; reaction temp, 140 °C and reaction time, 2h.

**3.2.2 Effect of reaction temperature**

Table 3 and (Fig.3) Shows the effect of reaction temperature (100-160°C) on the extent of modification when MCC particles was treated with BTCA. As is evident, the carboxyl content of cation exchanger increases from 52.1 to 248 m.eq/100 g sample by increasing the reaction temperature from 100 to160 °C. Enhancement of carboxyl content of cation

exchanger by increasing the reaction temperature from 100 to160 °C may be associated with the favorable effect of temperature on conversion of butane tetra carboxylic acid to Butane tetra carboxylic acid anhydride and reaction of the anhydride with cellulose hydroxyls of MCC particles to form cation exchanger

Table 3: Effect of reaction temperature on the extent of modification expressed as m.eq-COOH/ 100 g sample of cation exchanger

Reaction temperature (°C)	carboxyl content (m.eq/100g sample)
100	52.1
110	112.5
120	117.1
130	190.6
140	239.5
150	242.7
160	248

Reaction conditions: BTCA concentration, 8.54 m.mole / l and reaction time, 2h.

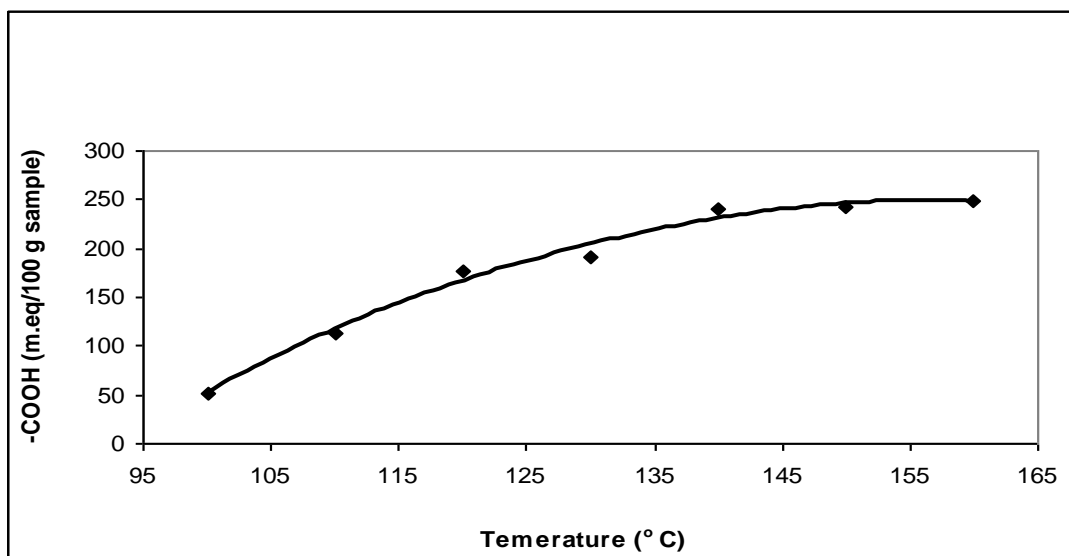


Fig. 3: Effect of reaction temperature on the extent of MCC modification  
Reaction Conditions: MCC, 2g; BTCA conc.,8.547 m.mole/l and reaction time,2h.

### 3.2.3 Effect of reaction time

Table 4 and (Fig.4) shows the variation of carboxyl content of cation exchanger with reaction time. It is clear from this table that, the carboxyl content of samples increases from 128.104 to 241.4 m.eq /100g sample by increasing the reaction time from 15 to

200 min. The increment in carboxyl content of cation exchanger by prolonging the reaction time is a direct consequence of the favorable effect (catalytic effect) of time on formation of BTCA anhydride which reacts with the cellulose hydroxyls of MCC to form cation exchanger.

Table 4: Effect of reaction time on the extent of modification expressed as m.eq-COOH/ 100 g sample of cation exchanger

Time (min)	carboxyl content (m.eq/100 g sample)
15	128.1
30	187.7
60	218.7
90	229.1
120	234.3
180	241.6
200	241.4

Reaction conditions: BTCA concentration, 8.54 m.mole / l; reaction temperature, 160 °C.

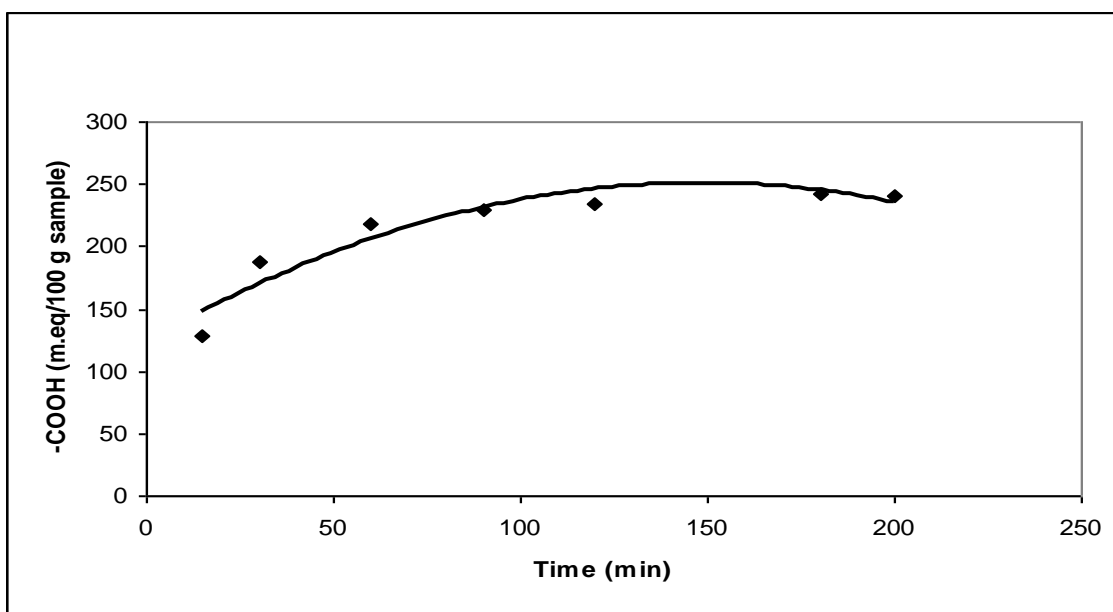


Fig. 4:Effect of reaction time on the extent of modification of MCC

Reaction Conditions: MCC, 2g; BTCA conc, 8.547 m.mole/l and reaction temp, 160°C.



**3.3. Factors affecting adsorption of Pb (II) onto cation exchanger**

**3.3.1 Effect of contact time**

Figure 5 shows the effect of reaction time and adsorbate concentration on adsorption capacity of Pb (II) by cation exchanger. The adsorption capacity (mg/g) increases by increasing the reaction time and concentration of adsorbate and remained nearly constant after equilibrium time. The equilibrium time increases by increasing the concentration of adsorbate. The equilibrium times are 5-120 min for adsorbate

concentration of 303.464 and 493.129 mg/l. It is clear that, the adsorption of pb (II) onto cation exchanger depends on concentration of adsorbate. The adsorption curves are singles and continuous leading to saturation. This data is important because equilibrium time is one of the parameters for economical wastewater treatment.

Table 5: Pseudo-second order adsorption rate constant and the calculated and experimental  $q_e$  of Pb (II) onto cation exchanger at 30°C

Adsorbent	Initial concentration of Pb(II) (mg/l)	Experimental $q_e$ (mg/g)	Calculated $q_e$ (mg/g)	Adsorption rate constant $K_2$ (g/mg min )	$R^2$
Cation exchanger	303.464	663.827	769.23	0.000547	0.994
	493.129	790.270	833.33	0.000993	0.998

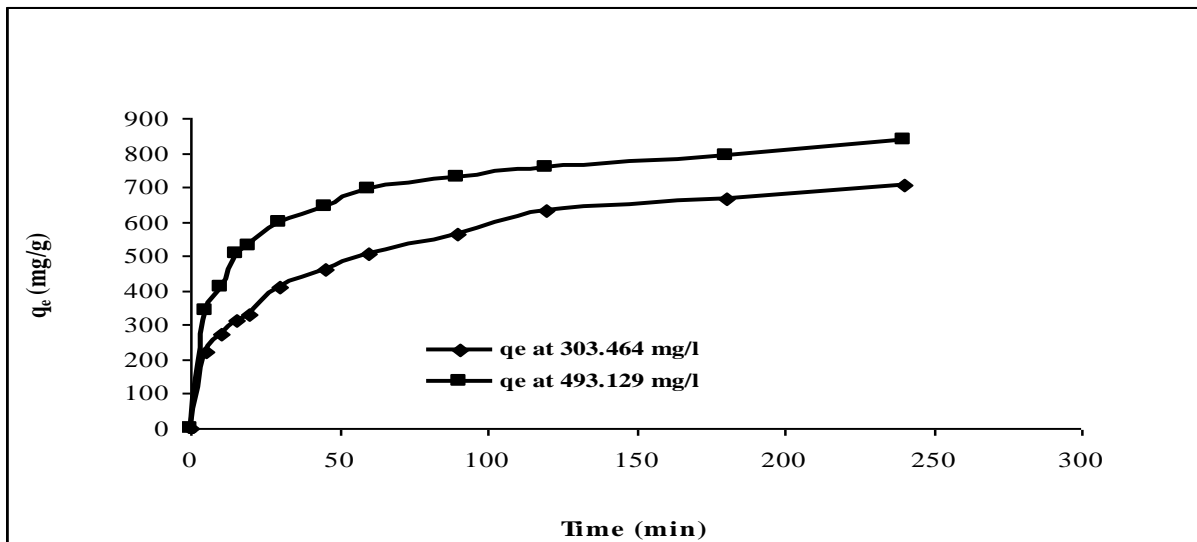


Fig. 5: Effect of reaction time and concentration on adsorption capacity of Pb (II) onto MCC treated by BTCA .

**3.3.1.1 Adsorption kinetics**

Several models have been proposed to express the mechanism of adsorption of Pb (II) onto cation exchanger as follows:

- (a) The pseudo-first-order kinetic model
- (b) The pseudo-second-order kinetic model
- (c) The intra-particle diffusion model

A pseudo- first order model of Lagergren as cited by Trivedi et al. (5) as follows :

$$\frac{dq}{dt} = k_1 (q_e - q_t) \tag{8}$$

where  $q_t$  (mg/g) is the amount of adsorbed metal ion on the adsorbent at time  $t$  and  $k_1$  ( $\text{min}^{-1}$ ) is the rate constant of the first-order adsorption. The integrated form of Eq. 8 is:

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \tag{9}$$

where  $q_e$  is the equilibrium adsorption capacity and extrapolated from the experimental data at time  $t = \text{infinity}$ .

The pseudo-second-order kinetic model (6) is expressed as:

$$\frac{dq}{dt} = k_2 (q_e - q_t)^2 \tag{10}$$

The integrated form of Eq. 10 is:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \tag{11}$$

Eq. 11 can be arranged and linearized to obtain :

$$\frac{t}{q_t} = \frac{1}{(k_2 \cdot q_e^2)} + \frac{t}{q_e} \tag{12}$$

where  $q_e$  and  $q_t$  are the amounts of metal ions adsorbed on the adsorbent at equilibrium and at time  $t$  (mg/g).  $k_2$  ( $\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$ ) is the rate constant of second-order adsorption.

The intra-particle diffusion model (7) can be written by the following:

$$q_t = K_p t^{1/2} + C \tag{13}$$

where  $C$  is the intercept and  $k_p$  is the intra-particle diffusion rate constant ( $\text{mg} \cdot \text{g}^{-1} \cdot \text{min}$

$^{-1/2}$ ). The straight line of plots of  $\log (q_e - q_t)$  versus  $t$  for the first-order reaction and  $t/q$  against  $t$  for the pseudo- second- order reaction (Fig. 6) for the adsorption of Pb (II) onto cation exchanger have been tested to obtain the kinetic rate parameters.

The kinetic parameters of Pb (II) onto cation exchanger at different time, and concentrations were calculated from the plots are shown in Table 5. The correlation coefficients,  $R^2$  for the first- order- kinetic model are between 0.215 and 0.971 for two concentrations used (figures and tables not shown) and the correlation coefficients,  $R^2$ , for the pseudo- second order kinetic model are over than 0.99 for two concentrations. It is probable, therefore, this adsorption system is not a first-order reaction. It fits the pseudo-second-order kinetic model.

The first-order and therfor pseudo-second-order models cannot identify the diffusion mechanism and the kinetic results were then subjected to analyze by the intra-particle diffusion model.

In the present study, it was found that, the plots of  $q_t$  versus  $t^{1/2}$  (Fig. 7) curved at a small limit times followed by linear portion and plateau. The initial curved portion of the plots seems to be due to boundary layer adsorption and the linear portion to intra-particle diffusion, while the plateau corresponding to equilibrium. Values of the intra-particle diffusion constant,  $k_p$  were obtained from the slopes of the linear portions of the plots (Fig.8) and are listed in Table 6. The correlation coefficients for the intra-particle diffusion ( $R^2$ ) were between 0.9969 to 0.9642 for two concentrations under investigation. The values of intercept,  $C$  (Table 6) give an idea about the boundary layer thickness i.e. the larger the intercept, the greater is the boundary layer effect (8). These values indicate that the adsorption of Pb (II) onto the cation exchanger may be follow the intra-particle diffusion mechanism.

Table 6: Rate parameters of intra-particle diffusion at different initial concentrations of Pb (II) onto cation exchanger at 30 °C

Adsorbent	Concentration of Pb (II) (mg/l)	$K_p$ (mg. g <sup>-1</sup> . min <sup>-1/2</sup> )	R <sup>2</sup>	Intercept C
cation exchanger	303.464	39.522	0.9969	159.5
	493.129	28.519	0.9642	455.04

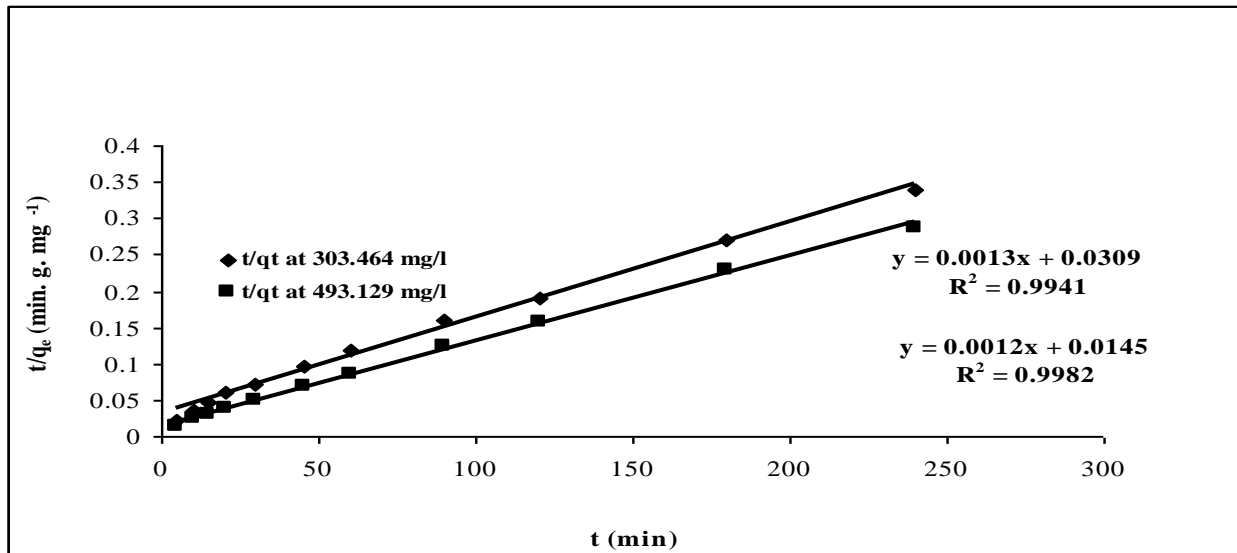


Fig. 6: Pseudo-second order reaction of Pb (II) onto MCC treated by BTCA at 30 °C .

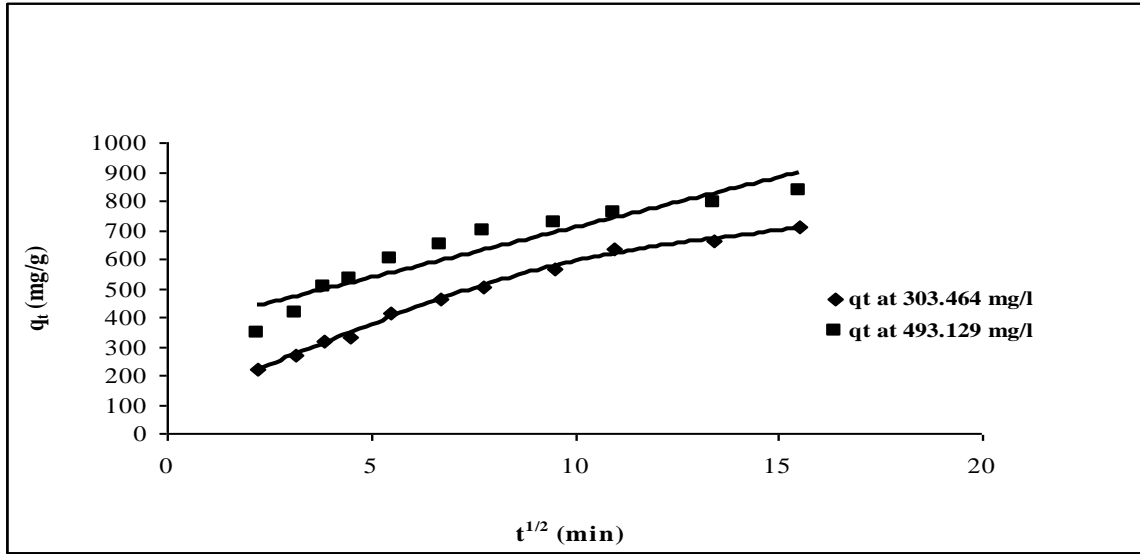


Fig. 7: Intra-particle diffusion of Pb (II) onto MCC treated by BTCA at concentrations of 303.464 and 493.129 mg/l.

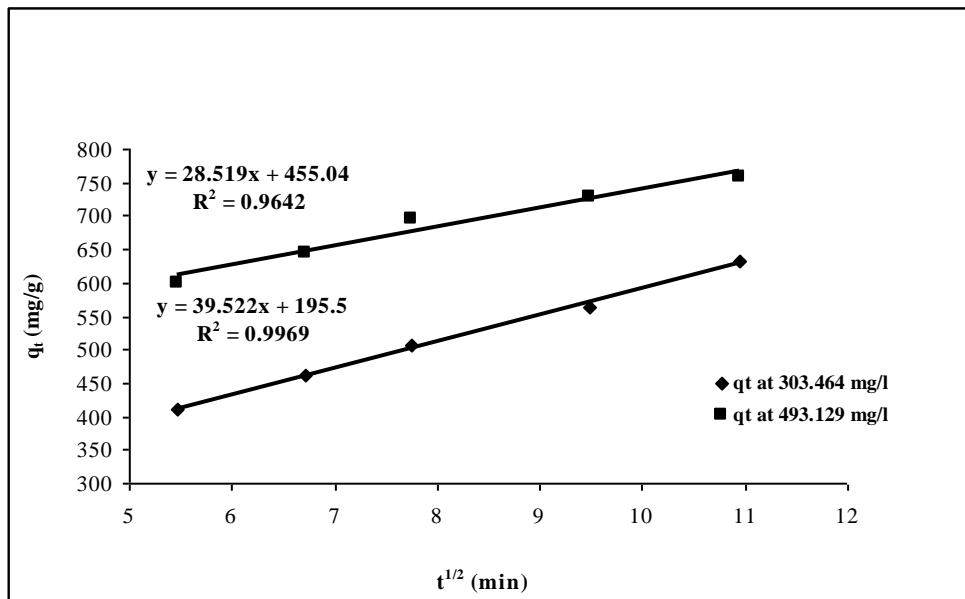
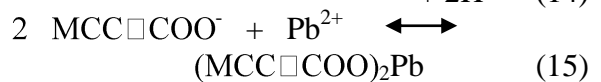
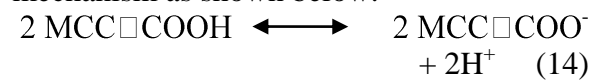


Fig. 8: Test intra-particle diffusion of Pb (II) onto MCC treated by BTCA at concentrations of 303.464 and 493.129 mg/l

**3.3.2 Effect of pH**

Figure 9 shows the effect of pH of adsorbate on the adsorption capacity,  $q_e$  of Pb (II) ions on cation exchanger at 30 °C and at pH range of 2- 4.5. The pH of the aqueous solution containing metal ions is an important controlling parameter in adsorption process <sup>(9)</sup>.

The Pb (II) ions are adsorbed on the surface of the cation exchanger by ion exchange mechanism as shown below:



Equation (14) represents deprotonation which is the first stage of ion exchange, while equation (15) represents the attachment or adsorption of the metal cation on the deprotonated surface. It is clear from Figure 9 that, the adsorption capacity,  $q_e$  of Pb (II) at pH 2 is 0. This is due to the fact that, at  $\text{pH} \leq 2$ , the high concentration of the  $\text{H}^+$  in solution shifts the equilibrium in equation (10) mainly to the left. This implies that, the active COOH groups are not deprotonated and therefore, the ion exchange sites on the cation exchanger surface are still protonated. As the pH increases from 2 to 4.5, the adsorption capacity of Pb (II) increases. The increase of  $q_e$  by increasing the pH up to 4.5 could be attributed to the ion exchange sites becoming increasingly ionized and the metal ions become adsorbed according to equation (14). At pH value higher than 4.5, the adsorption studied could not be carried out because the precipitation of lead ion in solution above this range.

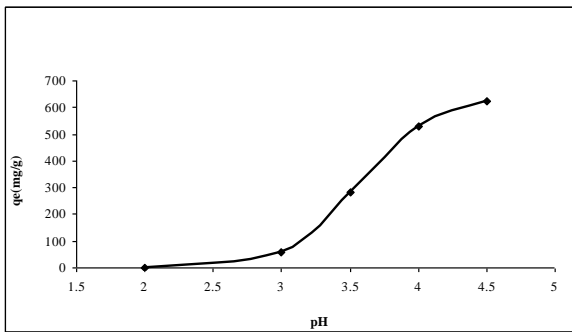


Fig. 9: Effect of pH on the adsorption capacity of pb(II) onto MCC treated by BTCA

### 3.3.3 Effect of adsorbent concentration

The effect of adsorbent concentration on both percent removal and adsorption capacity of Pb (II) onto cation exchanger were studied by varying the concentration of the adsorbent in the range of 0.3-8 g/l, at lead concentration, 400 mg/l; pH 4.5; temperature, 30 °C and contact time of 120 min. These results are shown in Table 7. The

results showed that with the increase in the adsorbent concentration, the percent removal of lead was increased. The increase in the percent removal with the increase in adsorbent concentration may be due to the increase in adsorbent surface area and availability of more adsorption sites <sup>(1)</sup>. But the adsorption capacity was decreased with the increase in adsorbent concentration (Table 7). As the adsorbent concentration was increased from 0.3 to 8 g/l, the adsorption capacity of Pb (II) was decreased from 695.4 to 38.4 mg /g. This may be due to overlapping of adsorption sites as a result of overcrowding of adsorbent particles <sup>(1)</sup>.

### 3.3.4 Effect of adsorbate concentration (Adsorption isotherm)

Adsorption data for wide range of adsorbate concentrations are most conveniently described by adsorption isotherms, such as the Langmuir or Freundlich isotherms. The adsorption isotherms of Pb (II) on cation exchanger at temperatures, 30, 50 and 60 °C are shown in Fig. 10. The Pb (II) uptake increased with increased temperature, thereby indicating the process to be endothermic.

#### 3.3.4.1 Langmuir isotherm

Langmuir equation <sup>(10)</sup> was applied for adsorption equilibrium at temperatures, 30, 50 and 60 °C. The assumption of this model is based on the maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on the adsorbent surface and the energy of adsorption is constant as well as there is no transmigration of adsorbate in the plane surface. The Langmuir isotherm is represented by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{(Q_{\max} \cdot b)} + C_e \quad (16)$$

where  $C_e$  is the equilibrium concentration of the adsorbate (mg / l),  $q_e$  is the amount of metal ion adsorbed (mg/g) and  $Q_{\max}$  and  $b$  are Langmuir constants related to maximum

adsorption capacity (mg/g) and energy of adsorption (l/mg), respectively. The Langmuir constants,  $Q_{max}$  and  $b$  for three temperatures were calculated from the slope and intercept of Eq. 12. The Langmuir equilibrium constant,  $K_L$  is obtained from the following equation:

$$k_L = Q_{max} \cdot b \tag{17}$$

The equilibrium constant,  $K_L$  may be used to determine the enthalpy of adsorption,  $\Delta H^\circ$ . The plots of  $C_e/q_e$  vs  $C_e$  are linear which show that, the adsorption of Pb (II) onto cation exchanger follow the Langmuir isotherm model (Fig. 11).  $Q_{max}$ ,  $b$  and  $R^2$  for three temperatures are presented in Table 8. High  $Q_{max}$  values (Table 8) also showed that, the cation exchanger adsorbent has high capacity to remove Pb (II) from aqueous solution.

The effect of isotherm shape has been discussed with a view to predict whether an adsorption system is favorable or unfavorable (Table 9). The essential feature

of the Langmuir isotherm can be expressed by means of  $R_L$ , a dimensionless constant referred to as separation factor or equilibrium parameter.  $R_L$  is calculated using the following equation <sup>(11)</sup>.

$$R_L = \frac{1}{(1 + b \cdot C_o)} \tag{18}$$

where  $C_o$  is the initial metal ion concentration (mg/l). The values of  $R_L$  (for three temperatures) according to the above equation are presented in Table 10. The adsorption process is favorable If the  $R_L$  values lie between 0 and 1. The  $R_L$  values of Pb (II) onto cation exchanger are between 0.327-0.126, 0.344-0.134 and 0.335-0.129 for 30, 50 and 60 °C, respectively and therefore, adsorption of Pb (II) onto cation exchanger are favorable. The validity of Langmuir model suggests the adsorption process to be monolayer (homogenous sites).

Table 7: Effect of adsorbent concentration on both adsorption capacity and percent removal of Pb (II) onto cation exchanger at 30 °C

Adsorbent concentration (g/l)	$q_e$ (mg/g)	% Removal
0.3	695.4383	50
0.5	474.1625	56.818
1	316.7406	75.909
2	164.0602	78.636
3	113.799	81.818
4	87.7201	84.091
5	73.9693	88.636
6	50.5773	72.727
7	49.3129	82.727
8	38.4072	73.636

Adsorption conditions: Pb(II) ion conc., 400 mg/l; pH, 4.5; agitation time, 2h; adsorption temperature, 30 °C; carboxyl content, 248 m.eq /100 g sample.

Table 8: Langmuir adsorption plots of Pb(II) onto cation exchanger at different temperatures

pH	Temp. (°C)	$a_L$ (l/mg)	$k_L$ (l/g)	$Q_{max}$ (mg/g)	b (l/mg)	$R^2$
4.5	30	0.006777	7.5312	1111.11	0.006777	0.9787
	50	0.006275	7.84313	1250	0.006275	0.9606
	60	0.006536	9.3372	1428.57	0.006536	0.9728

Table 9: Effect of separation factor,  $R_L$  on isotherm shape

$R_L$ value	Type of isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

Table 10:  $R_L$  values based on Langmuir equation of Pb (II) onto cation exchanger at different temperatures

Initial conc., $C_o$ of Pb (II) (mg/l)	$R_L$ values		
	Temp. (°C)		
	30	50	60
303.464	0.327164	0.344325	0.335183
417.263	0.261247	0.276371	0.268296
493.129	0.230312	0.244237	0.236793
578.478	0.203238	0.215985	0.209164
720.727	0.169942	0.181675	0.175111
796.593	0.156286	0.166705	0.161121
948.325	0.134648	0.14387	0.138923
1024.191	0.12593	0.134648	0.12997

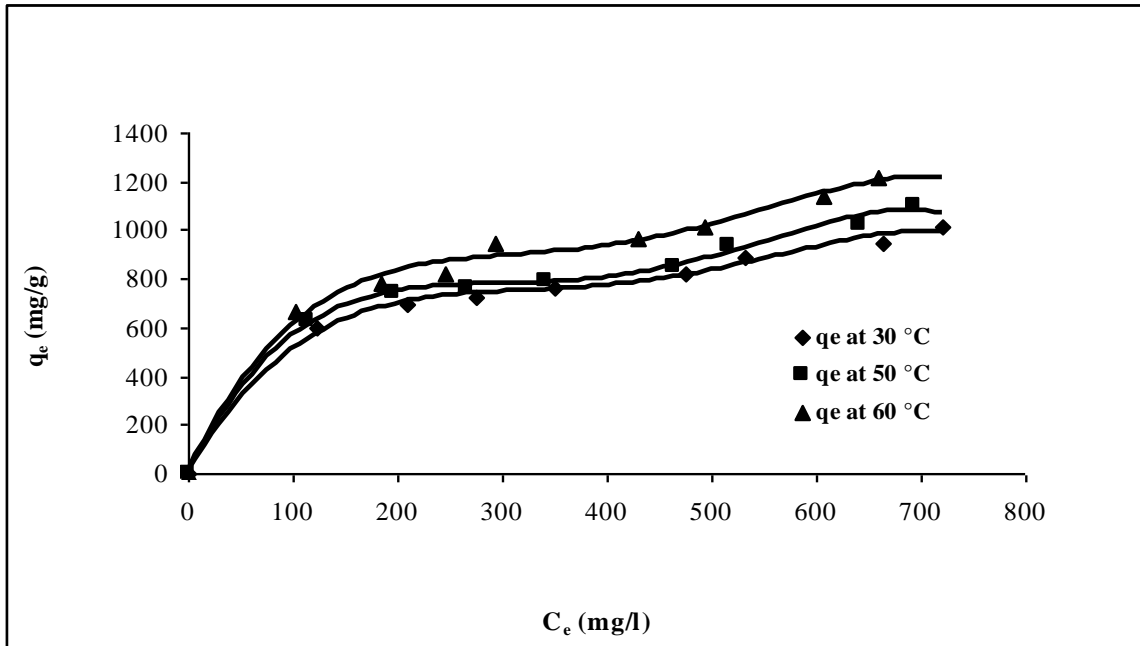


Fig. 10: Equilibrium adsorption isotherm of Pb (II) onto MCC treated by BTCA at different temperatures.

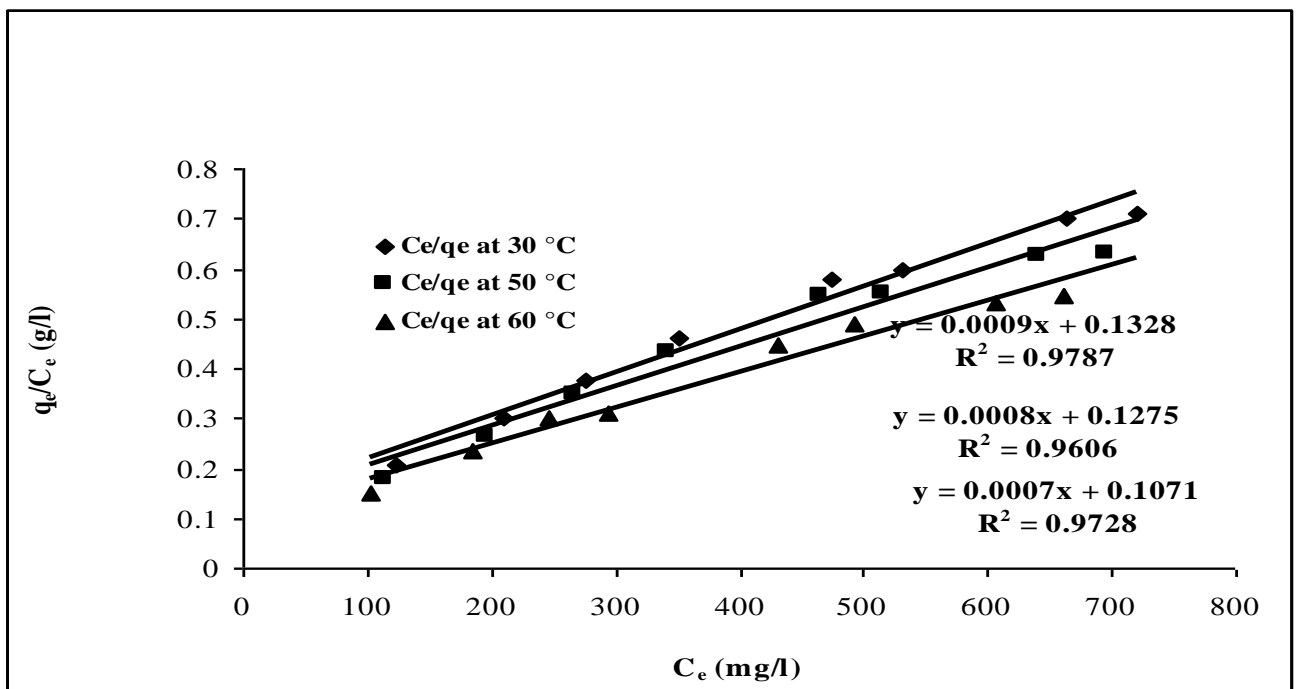


Fig. 11: Langmuir adsorption plot of Pb (II) onto MCC treated by BTCA. at defferent temperatures



**3.3.4.2 Freundlich isotherm**

The Freundlich adsorption isotherm was also applied for the adsorption of metal Pb(II) onto cation exchanger and is represented by the following equation <sup>(12)</sup>:

$$q_e = K_F \cdot C_e^{\frac{1}{n}} \quad (19)$$

where  $q_e$  is the equilibrium adsorption capacity of Pb (II) concentration onto cation exchanger, (mg/g),  $C_e$  the equilibrium concentration of Pb (II) in solution (mg/l) and  $K_F$  (mg /g) and  $n$  are the Freundlich constants characteristic of the system, indicators of adsorption capacity and adsorption intensity, respectively. The plots of  $\log q_e$  against  $\log C_e$  give as straight lines with the slope and intercept of which correspond to  $1/n$  and  $\log K_F$ , respectively. The Freundlich equation is employed to

describe heterogeneous systems and reversible adsorption and is not restricted to the formation of monolayer. Freundlich plots for Pb (II) onto cation exchanger at 30, 50 and 60 °C shown in Figure 12. The values of Freundlich constants for Pb (II) onto cation exchanger are listed in Table 11. The validity of Langmuir model suggests the adsorption process to be monolayer (homogeneous sites). However, the Langmuir model fitted slightly than Freundlich as evident from correlation coefficients (Table 8 and 11) suggesting mono layer coverage of adsorption, i.e. the experimental data were more fitted to the Langmuir equation than to the Freundlich equation.

Table 11: Freundlich constants of Pb (II) onto cation exchanger at different temperatures

pH	Temperature (°C)	$K_F$	$n$	$R^2$
4.5	30	154.134	3.590664	0.9683
	50	161.584	3.544842	0.9295
	60	161.882	3.307972	0.9588

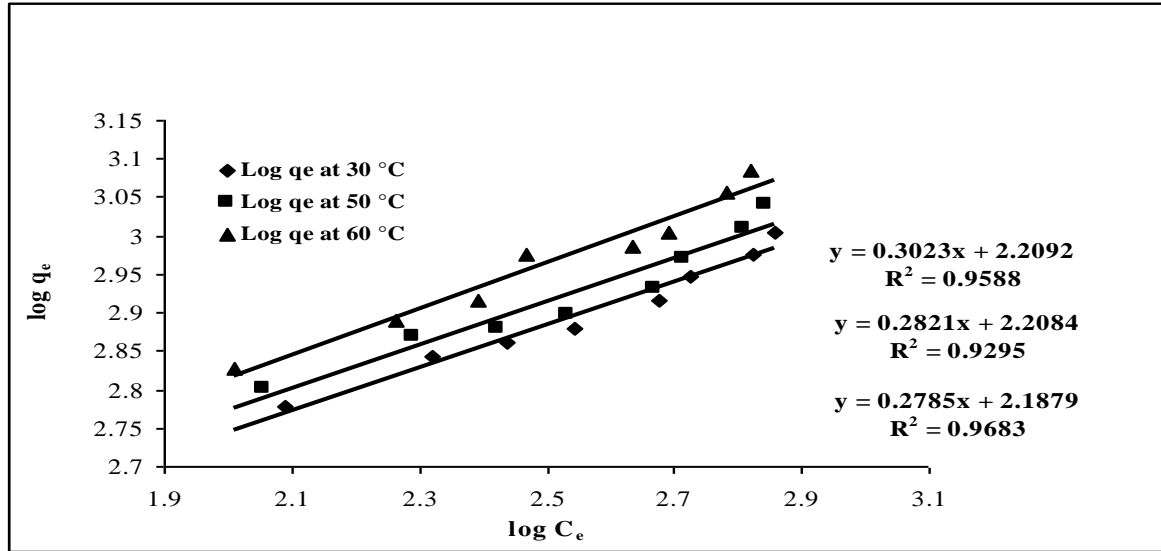


Fig. 12: Freundlich adsorption plot of Pb (II) onto MCC treated by BTCA at different temperatures .

### توصيف مبادلات كاتيونية مبنية علي مايكرو سيلولوز وتطبيقاتها

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#### المستخلص

تما تحضير مبادلات كاتيونية جديدة ناتجة من تفاعل ميكروكربستالين سيلولوز مع بيوتان رباعي حمض الخليك عند درجات الحرارة العالية وذلك عن طريق دراسة كل العوامل المؤثرة على عملية التفاعل وهي:-

تركيز التفاعل ، زمن التفاعل ودرجة الحرارة

وقد تم توصيف عينات المبادل الكاتيوني الناتج عن طريق دراسة طيف الأشعة تحت الحمراء و مقارنته ميكروكربستالين سيلولوز غير معالج.

وكذلك من خلال تقدير محتوى الكربوكسيل و تقدير النسبة المئوية للذوبان في الماء المقطر للمبادل الكاتيوني المحضر.

تم استخدام المبادل الكاتيوني المحضر لإزالة أيونات الرصاص الثنائي من المحاليل المائية عن طريق الإدمصاص.

وقد تم دراسة كل العوامل المؤثرة على عملية إدمصاص الرصاص للمبادل الكاتيوني المحضر و كانت هذه العوامل هي :-

تأثير تركيز أيون الهيدروجين للمحلول ، تركيز المادة المدمصة في المحلول ، الزمن ودرجة الحرارة

وقد أظهرت نتائج الإدمصاص أن المبادل الكاتيوني له المقدرة العالية في إزالة أيونات الرصاص الثنائي من المحاليل المائية. النتائج المتحصل عليها كانت تنطبق على نموذج لانجمير و فرنديش.

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