# REMOVAL OF 1-CHLORO-4-NITROBENZENE FROM AQUEOUS SOLUTIONS BY ADSORPTION ONTO BLACK TEA LEAVES WASTE

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## Abstract
Adsorption of 1-Chloro-4-nitrobenzene from aqueous solutions by black tea leaves waste as a low cost adsorbent has been carried out. The adsorption experiment were performed under various conditions such as different initial 1-Chloro-4-nitrobenzene concentrations, pH, dosage of black tea leaves waste, temperature and reaction time. It was found that adsorption reached equilibrium at 50 min and the optimum pH was found to be 7. Experimental results show that the kinetic model of pseudo second order provided a good description

*Keywords*- Adsorption, Kinetic, Black tea leaves waste, 1-Chloro-4-nitrobenzene

## I. INTRODUCTION
Benzoic compounds have been used for a number of years as a raw material in the manufacture of dyes, resins and detergents. To protect water sources, it is important to keep the concentrations of benzene in ground water as low as possible[1]. So many advanced methods such as chemical reduction, ion exchange, reverse osmosis and etc are sued for the treatment of wastewater [2]. These processes have been found to be limited, because they often involve high capital and operational costs [3] and also, these methods become inefficient when pollutants are present in trace concentration [4] and do not seem to be economically feasible [5]. So, there is necessary to look into alternative methods to investigate a low-cost method which is effective and economic.
Adsorption is one of the physico-chemical treatment processes and is an effective purification and separation technique used in industry especially in water and wastewater treatments in removing pollutants from aqueous solutions [6].This process can be considered as a cheap method [7] and the design is simple and has involve low costs. Several authors have reported studies on various low cost adsorbents such as wool, rice, straw, coconut husks, peat moss [8], walnut skin, coconut fiber [9] and cotton seed hulls [10-11]. After water, tea is the most widely consumed beverage in the world [12]. Many investigations have been conducted to test tea waste.
Mahavi et al. [13] used tea waste as an adsorbent for the removal of heavy metals (Cd, Pb, Ni) from industrial waste. About 94-100% removal of lead, 86% for Ni and 77% for Cd were achieved using tea waste. The adsorption ability of tea waste were investigated for the removal of Cu(II) and Cd(II) from non-competitive and competitive aqueous systems [14-15]. Malkoc and Nuhoglu [15] studied the removal of nickel from aqueous solution using tea factory waste (TFW).
This paper report the effect of pH, contact time, black tea leaves waste (BTLW), initial concentration and temperature on 1-Chloro-4-nitrobenzene sorption by using black tea leaves waste.

## MATERIALS
1-Chloro-4-nitrobenzen (1C4NB) [$C_6H_4ClNO_2$, M=157. 6 g $mol^{-1}$; λmax=280 nm] (Fluka Co.) was selected as a model compound. A stock solution of 1-Chloro-4-nitrobenzene was prepared at a concentration of approximately 20 mg/L. Black tea leaves waste used as adsorbent. All solutions were prepared by using deionized water. All other chemicals were reagent grades and were supplied from Merck, Germany.

## METHODS
The adsorption of 1C4NB from aqueous solution onto Black Tea Leaves Waste (BTLW) was performed using batch equilibrium technique. All of the adsorption experiments were conducted in a 250 mL erlyn mayer on the magnetic stirrer. The effect of BTLW on the amount of 1C4NB adsorbed was investigated as a function of initial concentration of 1C4NB(5, 10, 15 and 20 mg/L), pH (3,7 and 12) and BTLW dosage (1, 2, 3, 4 and 5 g/250 mL ). The pH of the solution was adjusted using HCl and NaOH. Following sampling at predetermined time intervals (each 10 min), suspensions were centrifuged and the 1C4NB concentrations were measured using a UV-Vis spectrophotometer (HACH-DR5000) at wavelength corresponding to maximum absorption (280 nm).

The adsorption yield (%), the adsorbed 1C4NB amount onto the BTLW (mg/g) at any time ($q_t$) and at equilibrium ($q_e$), were calculated from the following equations (1-3), respectively:

$$\text{Removal}\ (\%) = \frac{C_t - C_0}{C_0} \times 100 \qquad (1)$$

$$q_t = \frac{(C_0 - C_t)}{M} V \qquad (2)$$

$$q_e = \frac{(C_0 - C_e)}{M} V \qquad (3)$$

where $C_0$, $C_t$ and $C_e$ are the initial, at any time and equilibrium 1C4NB concentration (mg/L), respectively. V is the solution volume (L) and M is the adsorbent mass (g).

## RESULTS AND DISCUSSION

### EFFECT OF CONTACT TIME

The effect of contact time on 1C4NB adsorption at initial concentration of 20mg/L was investigated as shown in Fig 1. It was observed that the rate removal of 1C4NB was rapid initially but it gradually decreased with time until it reached equilibrium at about 50 minutes. So, in all experiments the contact time was 50 min.

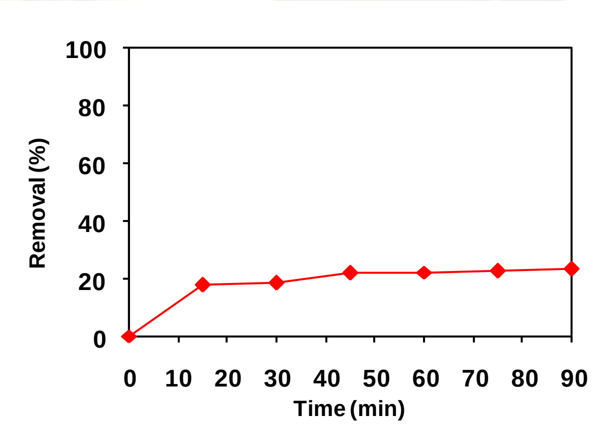


Fig 1.Effect of contact time on 1C4NB adsorption onto BTLW
$[1C4NB]_0$=20mg/L;[BTLW]=3g/250mL;pH=6;T=25$^{\circ}$C

### EFFECT OF PH

pH plays a mean role in the phenomena of adsorption. So, it is necessary to examine the influence of the pH of the solution on the adsorption yields. In this research the effect of pH investigated at pH 3, 7 and 10 and all other operative conditions remained constant ($[1C4NB]_0$=20mg/L;[BTLW]=1g/250mL;Contact time=50 min.;T=25$^{\circ}$C)
Fig. 2 represents quantities of 1C4NB adsorbed, at equilibrium, at pHs 3, 7 and 10.
At a strongly acidic pH (pH = 3), the adsorption is relatively low, followed by a strong increase until a pH of 7 where the adsorption is maximal. At pH=9, adsorption more decreased. The results show that isoelectric point of BTLW is around pH=7 ( not shown here). Over this point the surface of BTLW is charged negatively and under it is positive. Since 1-chloro-4-nitrobenzene is a kind of unionizable compound, the adsorption density is consistent with the concentration of the natural surface sites of BTLW ,i.e., around pH=7. It implies that 1C4NB will be adsorbed by the greatest extent on BTLW surface under conditions in which pH = pHzpc[16].

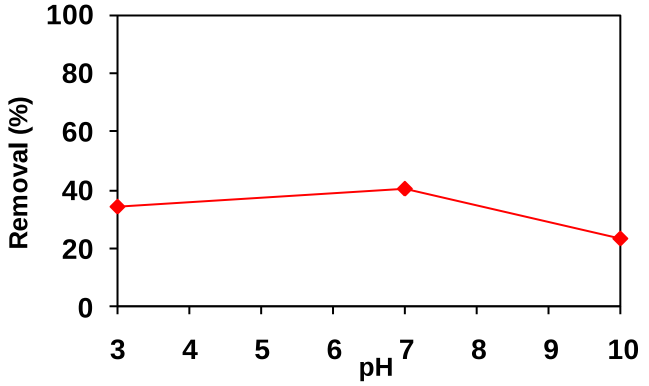


Fig. 2: Effect of pH on 1C4NB adsorption onto BTLW
$[1C4NB]_0$=20mg/L;[ BTLW]=1g/250mL;T=25°C

In conclusion, we note that the adsorption is favoured around the pH= 7.

## EFFECT OF THE INITIAL CONCENTRATION OF 1C4NB

To determine the effect of the concentration on the adsorption of 1C4NB (5,10,15,20 mg/L) in aqueous solution in contact with BTLW, the variation of the quantity of 1C4NB adsorbed has been examined. The results is shown in Fig. 3, which shows that the initial concentration has influence on the amount of 1C4NB absorbed on BTLW.At higher concentration, lower adsorption yield is due to the saturation of adsorbent sites which is a consequence of increase in the number of 1C4NB molecules competing for available binding sites of BTLW[2].

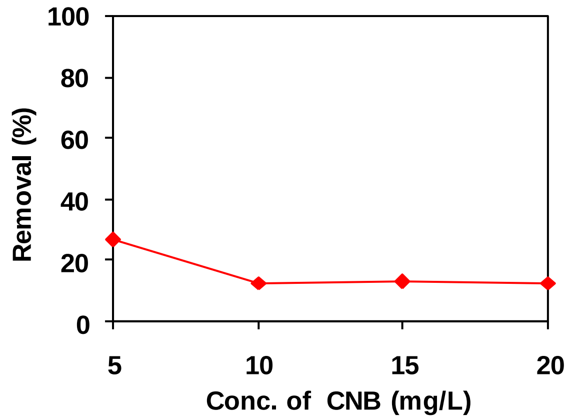


Fig. 3: Effect of initial 1C4NB concentration
[BTLW]=1g/250mL;pH=6;T=25°C

## EFFECT OF BTLW DOSAGE

Effect of BTLW dosage on the amount of 1C4NB adsorption was studied at constant pH. Based on the results (Fig. 4), increasing adsorbent concentration increased the percent adsorption. An increase in the adsorption with the increase of adsorbent dosage from 1 to 5 g/250 mL can be attributed to greater surface area and the availability of more adsorption sites [17].

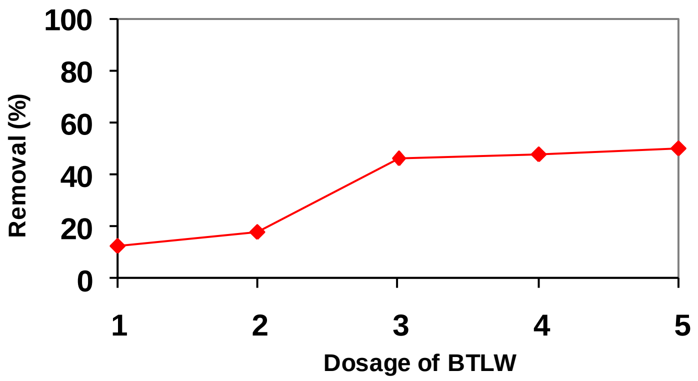


Fig. 4: Effect of dosage of BTLW
$[1C4NB]_0$=20mg/L: pH=6;T=25°C

## EFFECT OF TEMPERATURE

To determine the effect of temperature on the adsorption of 1C4NB by BTLW, the experiments were performed at temperatures of 20, 30 and 40 °C. It is clear from Figure 5, that the adsorption onto BTLW was decreased by increasing the temperature from 20 to 40°C, indicating that adsorption of 1C4NB on BTLW is an exothermic process. A decrease in the adsorption of 1C4NB with the rise in temperature may be explained by being more active adsorbing sites at low temperature [18].

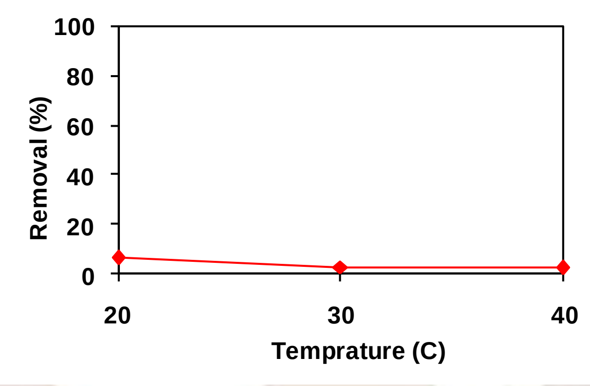


Fig. 5 : Effect of temperature
[BTLW]=1g/250mL; $[1C4NB]_0$=20mg/L: pH=6;T=25°C

## ADSORPTION KINETIC STUDIES

In order to find out the potential rate-controlling steps involved in the process of adsorption of 1C4NB, both pseudo first-order and pseudo second order kinetic models were used.

## PSEUDO-FIRST ORDER MODEL

The pseudo-first-order model was described by Lagergren as[19]: $Ln(q_e - q_t) = Lnq_e - k_1 t$

Where $q_e$ (mg/g) and $q_t$ (mg/g) are the amount of 1C4NB adsorbed at equilibrium and at any time and $k_1$ (1/min) is the rate constant of pseudo-first-order adsorption. A linear plot of Ln (qe − qt) against time can be used to calculate the rate constant.

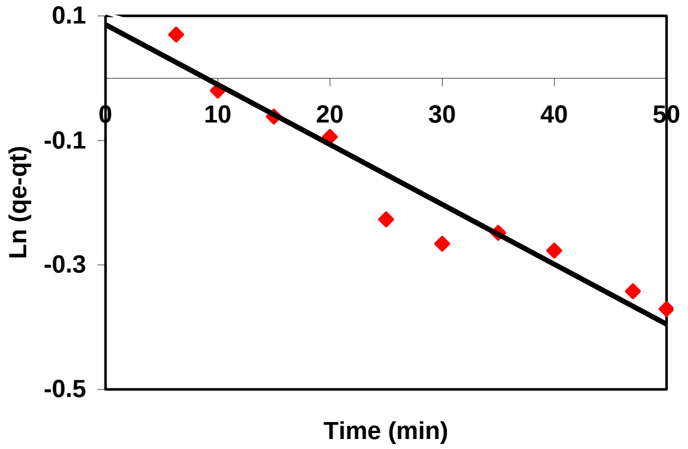


Fig. 6: Pseudo first order kinetic plot for adsorption of 1C4NB on BTLW adsorbent

## PSEUDO-SECOND ORDER MODEL

pseudo-second order kinetic model [19] is expressed in its linear form as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right) t$$

Where:

t = time, min

$q_t$ = 1C4NB concentration in the solid phase at time t, mg $g^{-1}$

$K_2$ = pseudo-second order rate constant, g $mg^{-1}$ $min^{-1}$

Values of $q_e$ and $K_2$ can be obtained from the slope and intercept of the plot $t/q_t$ vs. t.

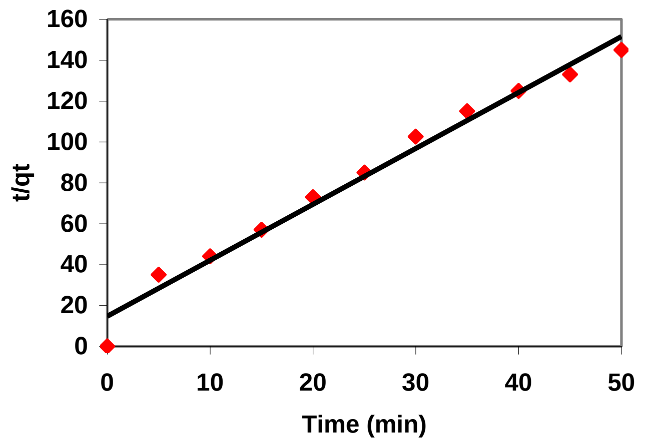


Fig. 7: Pseudo second order kinetic plot for adsorption of 1C4NB on BTLW adsorbent

In Figs. 6 and 7 the plots of adsorption kinetic models is shown. The results of the kinetic parameters for 1C4NB adsorption on BTLW are listed in Table 1.

Table 2: Kinetic parameters for 4C2NP adsorption onto nano-$TiO_2$

| Pseudo-first-order model | | Pseudo-second-order model | |
|---|---|---|---|
| $k_1$ ($min^{-1}$) | $R^2$ | $k_2$ (L $mol^{-1}$ $mim^{-1}$) | $R^2$ |
| 0.009 | 0.9503 | 0.509 | 0.9808 |

The coefficient of determination, $R^2$, for the pseudo-second-order adsorption model has a high value. These facts suggest that the pseudo-second-order adsorption mechanism is predominant.

## CONCLUSION

The present investigation shows that the BTLW is an effective and inexpensive adsorbent for the removal or 1C4NB from aqueous solutions. Results show that the equilibrium time period for removal of 1C4NB onto BTLW adsorbent is 50 min and the maximum removal of the 1C4NB occurs at pH= 7. The pseudo first order and pseudo second order models were used to describe the kinetic data. The adsorption followed the pseudo second-order kinetics. Effect of temperature on adsorption of 1C4NB onto BTLW show that adsorption is an exothermic process.

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