Benzoic Compounds Removal from Aqueous Solutions by Acidic Silk: Equilibrium and Kinetic Study

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A-B-S-T-R-A-C-T

Background & Aims of the Study: p-Chloronitrobenzene is a benzoic compound that widely used in many chemical industrials. p-Chloronitrobenzene may be absorbed through the skin and is suspected to causing cancer. So, developing an easy method to remove of it from the environment is necessary. Equilibrium isotherms and adsorption kinetics of p-Chloronitrobenzene onto modified silk waste were studied experimentally.

Materials and Methods: Silk waste was modified by HCl and used as an adsorbent to remove of p-Chloronitrobenzene from aqueous solutions. After preparing of adsorbent, the adsorption experiments were down in a batch system in an erlen mayer at different concentrations of p-Chloronitrobenzene (20, 40, 60, 80, 100 mg/L), pH (2, 4, 6), dosage of modified silk waste (1, 2, 3, 4, 5 g/250 mL), temperature (20, 30, 40 $^\circ$C) and contact time.

Results: Data revealed that the adsorption of p-Chloronitrobenzene on to modified silk waste was reached equilibrium after 20 min. The adsorption of p-Chloronitrobenzene decreased with the increasing of pH and the concentration of p-Chloronitrobenzene which is increased by increasing of modified silk waste dosage. Also, data confirmed that changing of temperature did not have significant p-Chloronitrobenzene removal efficiency. Pseudo-first-order and pseudo-second-order equations were used to determine the kinetics of removal process. It was found that the adsorption of p-Chloronitrobenzene onto modified silk waste was obeyed from pseudo-second-order kinetic model.

Conclusion: The results indicated the adsorption of p-Chloronitrobenzene onto modified silk waste could be well fitted with the Freundlich isotherm and pseudo-second-order kinetic models.

Background

Nowadays, pollution of water by chemical waste is a very serious problem. One of the hazardous chemical pollutants is benzoic compounds that widely used in dyes, resins and industries (1). As previous studies, benzoic compounds are penetrated through the skin and damage of lung and kidney (2). Due to these risks, benzoic compounds must be removed from the environment especially aqueous environments (3). Many studies tried to remove of benzoic compounds, using chemical and physical methods (4). One of the simple and cheap methods is adsorption. Various adsorbents such as activated carbon, metal oxides, hydroxides, alumina, clays etc. which were used for treatment of water and wastewater (5). Todays, using of natural adsorbents such as banana pith (6), coconut husk (7), sawdust (8), cotton (9), fiber (10), kenaf (11), vegetable fibers (12) and wool (13) are in interests. Due to environmentally friendly and reusability properties of natural adsorbents,

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they are very attractive in adsorbtion of pollutants.

Aims of the study:

The aim of this paper is the study the modified silk waste (MSW) as a cheap and green adsorbent to remove p-Chloronitrobenzene (pCNB) from aqueous solutions. In addition, the effect of contact time, pCNB concentration, pH, MSW dosage and temperature was studied. Also, kinetic and equilibrium isotherms were analyzed.

Materials & Methods

Materials

p-Chloronitrobenzene (pCNB) was purchased from Fluka Co. Silk waste which was prepared from Arasbaran, Iran Jungle and was used as an adsorbent. Other chemicals were purchased from Merck, Germany.

Preparation of adsorbent

Firstly, the silk waste was washed by distilled water for three times and then it was dried in an oven at 60 °C. To evaluate the efficiency of MSW, pieces of MSW are modified by immersing in HCl solution for about 24 h. Then it was washed thoroughly with deionized water to be naturalized and dried under vacuum at room temperature. The dried modified silk waste was cut into small pieces and used as an economic adsorbent.

Methods

All experiments were done in a batch system, using pCNB as pollutants and MSW as an adsorbent in an erlenmayer on the shaker. Efficiency of MSW on removal of pCNB was studied as a function of concentration of pCNB (5, 10, 15 and 20 mg/L), pH (2,4 and 6), MSW dosage (1, 2, 3, 4 and 5 g/250 mL) and different temperatures (20,30,40 ºC). HCl and NaOH were used for adjustment of pH. Samples were shaken at 140 rpm and sampling was taken every 10 min. It was filtered by 0.2μm syringe filter and the pCNB remained concentration was recorded, using a UV-Vis spectrophotometer (HACH-DR5000) at 280 nm (maximum absorption wavelength). Following

equations (1-3) were used to calculate of pCNB removal, adsorbtion of pCNB onto the MSW (mg/g) at any time (q_t) and at equilibrium (q_e), respectively.

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

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

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

Where, C_0, C_t and C_e are initial at any time and equilibrium concentration of pCNB (mg/L), respectively. V is solution volume (L) and M is adsorbent mass (g).

Results

Effect of contact time

Equilibrium time is a very important in adsorption process. In order to obtain the equilibrium time of pCNB adsorption onto MSW, removal of pCNB onto MSW was analyzed in various contact times and results are shown in Fig. 1.
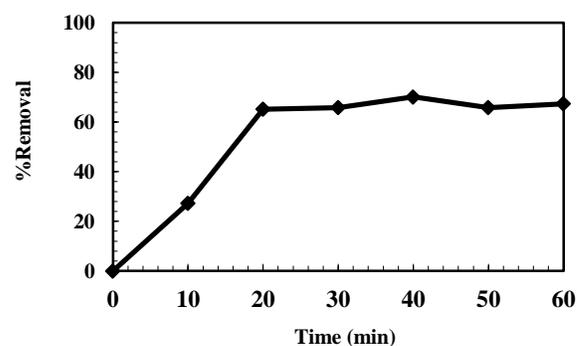

Figure 1) Effect of contact time
[pCNB]₀=20mg/L;[MSW]=3g/250mL;pH=6;T=25ºC

Effect of pH

pH is one of the key factors in adsorption phenomenon. To study the effect of pH on MSW efficiency in removal of pCNB, 250 mL of pCNB (20mg/L) was prepared at various pHs (2,4,6) and in contact with the constant amount of MSW. Whereas, by increasing of pH, silk dissolve in water, so, acidic conditions were studied. Removal percent of pCNB at

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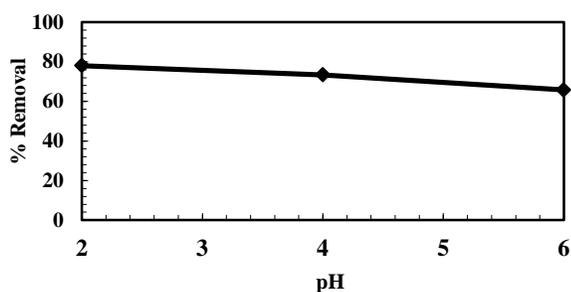equilibrium time, at pHs of 2, 4 and 6 is illustrated in Fig. 2.

Figure 2) Effect of pH
[pCNB]$_0$=20mg/L;[MSW]=3g/250mL;T=25ºC

Effect pCNB of concentration
Experiments were down in different concentration of pCNB (20, 40, 60, 80, 100 mg/L) to study the effect of initial concentration of pCNB and results are shown in Fig. 3.
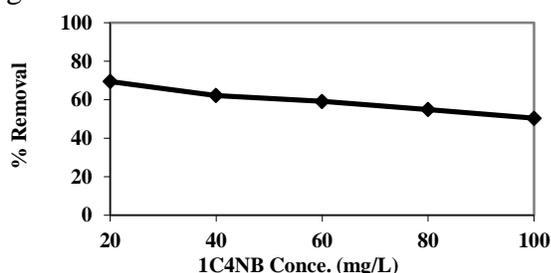

Figure 3) Effect of initial pCNB concentration
[MSW]=3g/250mL; pH=6;T=25ᵒC

Effect of MSW dosage
To investigate the MSW dosage on pCNB adsorption at constant pH, various amount of MSW were studied. As shown in Fig 4, increasing of adsorbent dosage leads to increase adsorption of pCNB onto MSW.
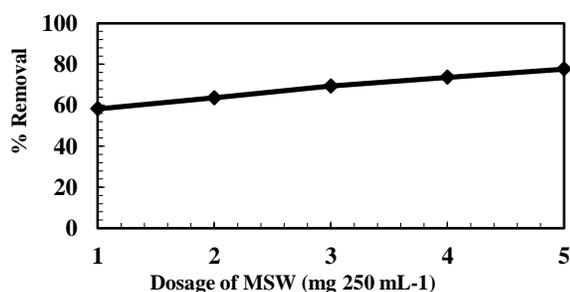

Figure 4) Effect of dosage of MSW
[pCNB]$_0$=20mg/L: pH=6;T=25ᵒC

Effect of temperature
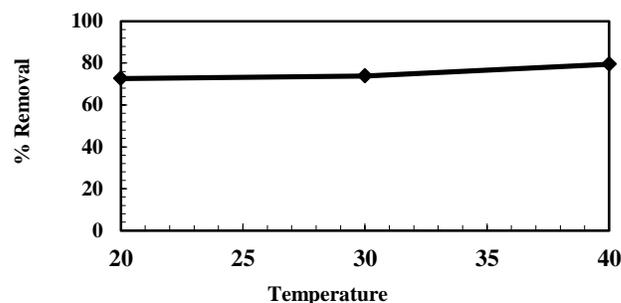Experiments were performed at different temperatures (20, 30 and 40°C) to study the effect of temperature (Fig. 5).

Figure 5) Effect of temperature
[MSW]=3g/250mL; [pCNB]$_0$=20mg/L: pH=6

Isotherm studies
To study of equilibrium isotherms, Langmuir, Freundlich and Temkin isotherm models were evaluated (21). The linear form of Langmuir, Freundlich and Temkin equations are given by Eqs. 4-6, respectively.

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L}\frac{1}{C_e} \tag{4}$$

$$\ln q_e = \ln K_f + \frac{1}{n}\ln C_e \tag{5}$$

$$q_e = B \ln K_T + B \ln C_e \tag{6}$$

In these equations, parameters were defined as following:

K_L=adsorption equilibrium constant (L/mg), q_m=maximum adsorption capacity (mg/g), C_e=equilibrium pCNB concentration (mg/L) and q_e=amount of adsorbed pCNB at equilibrium (mg/g). K_f=sorption capacity of the adsorbent (mg/g (L/mg)), n=an indication the favorability of the sorption process. If n>1, the adsorption is favorable. B=constant of Temkin (J/mol), K_T=constant of Temkin isotherm (L/g). Langmuir, Freundlich and Temkin isotherms of adsorption of pCNB onto MSW are shown in Fig. 6. Table 1 represents the isotherm constants.
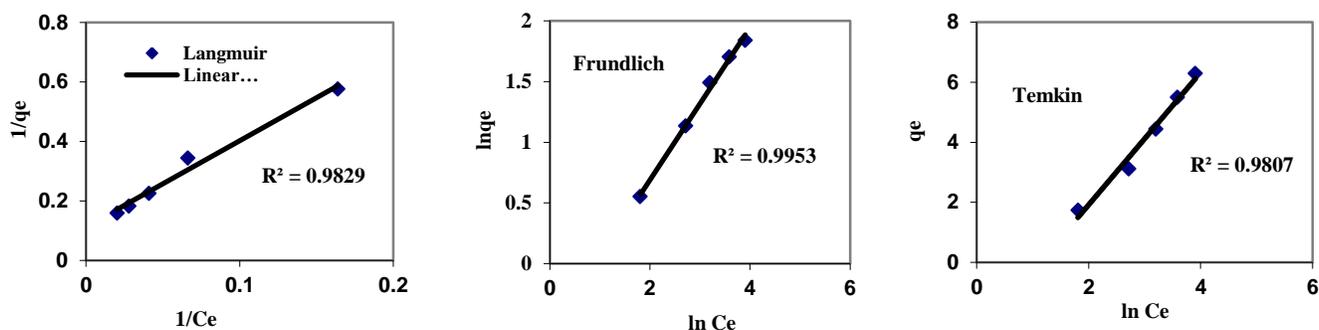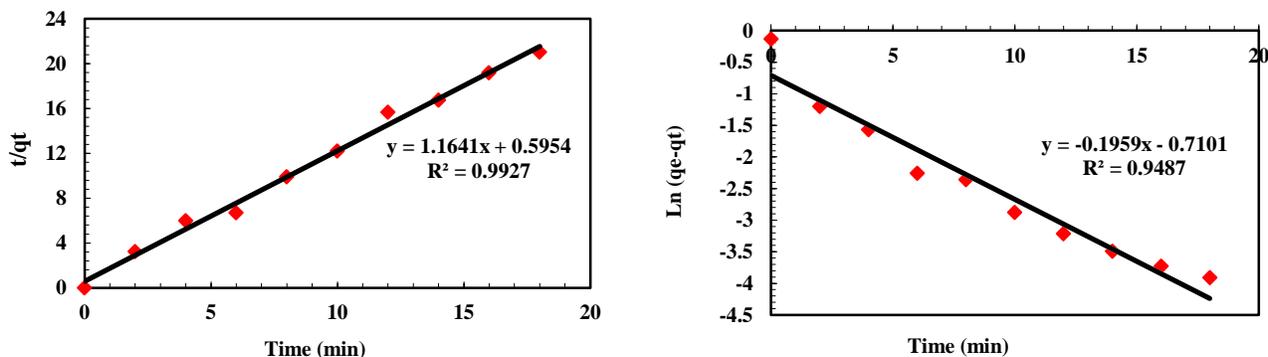

Figure 6) Isotherms adsorption of pCNB onto MSW

Table 1) Constants of the linear form of the Langmuir, Freundlich and Temkin isotherms

Langmuir Isotherm			Freundlich Isotherm			Temkin Isotherm		
q_m	K_L	R^2	K_f	n	R^2	B	K_T	R^2
9.201	0.037	0.982	0.56	1.59	0.995	2.203	0.270	0.980

Table 2) Kinetic parameters for pCNB adsorption onto MSW.

Pseudo-first-order model			Pseudo-second-order model		
q_e (mg/g)	k_1 (1/min)	R^2	q_e (mg/g)	k_2 (g/mg.mim)	R^2
0.491	0.195	0.948	0.859	2.29	0.992

Figure 7) Pseudo first order (left) and Pseudo second order (right) kinetic plot for adsorption of pCNB on MSW

Adsorption Kinetic Studies

Pseudo first-order and pseudo second order kinetic models were examined to study the kinetic of pCNB adsorption onto MSW.

Pseudo-First Order Model

The linear form of pseudo-first-order model is described as (24):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (7)$$

Pseudo-Second Order Model

The linear form of pseudo-second order kinetic model (24) is presented as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right)t \qquad (8)$$

q_e (mg/g) and q_t (mg/g) are the amount of pCNB adsorbed at equilibrium and at any time. k_1 (1/min) and k_2 (g/mg.min) are the rate constant of pseudo-first-order and pseudo-second order rate constant adsorption, respectively. The results of adsorption kinetic models are shown in Figs. 7 and Table 2.

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Table 3 shows the removal percent of pCNB by different adsorbents. As shown, Single Walled Carbon Nano tubes can be used such as an efficiency adsorbent to remove IC4NB from aqueous solutions.

Table 3) compare of different adsorbent in removal of pCNB

Adsorbent	% Removal
Black Tea Leaves Waste (25)	50%
Single Walled Carbon Nano tubes (26)	95.71%
Carbon nanofibers (27)	90%
Multi-Walled Carbon Nanotubes (28)	83.50%

Discussion

From Fig. 1, it can be seen that the rate of pCNB removal was rapid initially, then it drops. The equilibrium was achieved at about 20 minutes. So, all of experiments were followed during 20 min. As reported, in the initial times the number of available sites for adsorption is high and increasing of time due to saturated of those sites and adsorption reaches to equilibrium (1).

Fig. 2 shows by decreasing of pH, removal percent of pCNB was increased and raised from 65.76% to 78.10%. Generally, the adsorption of pCNB onto MSW is favored around the pH=2. Zeta potential charge (pHzpc) for MSW is obtained 2.3 (not shown here). For this, 0.1 g of MSW was dispersed in 1 L distilled water and the initial pH was monitored. Then, the pH of solution was adjusted with HCl or NaOH (pH 2–12) (14). As known at solution pH was less than the pHzpc, the surface charge is positive and at higher level of pHzpc, the surface charge is negative. At pH= pHzpc=2.3, there is no charge on the surface of MSW and pCNB is a unionizable compound (14). So, pCNB will be adsorbed by the maximum extent on the adsorbent surface at pH=2.3. Similar studies shown that adsorption of indigo carmine onto silk was reached to maximum at pH=3 and was decreased by increasing of pH (15).

Varying the initial concentrations of pCNB shows that (Fig. 3), increasing of pCNB due to low yield in removal efficiency. In fact, competing of pCNB molecules to adsorption onto active sites of MSW was increased and adsorbent sites were saturated (4). As known, there are limited vacant sites for adsorption, so, by increasing of pCNB molecules, the sites were full and the adsorption was dropped (16-17). Similar results were obtained by Heravi (18) that adsorption of direct red 81 onto modified silk was decreased from 97.75 to 60.3% by increasing of dye concentration from 40 to 100 ppm.

As Fig. 4, rising of adsorption by increasing of adsorbent dosage from 1 to 5 g/250 mL can be related to increase of surface area and available adsorption sites (19,20). As reported, dye removal efficiency was increased by increasing the modified silk dosage as results of the existence of more active sites (18).

Fig. 5 illustrates that there is no significant evidence by varying temperature. So, the change of temperature has no effect on removal efficiency and room temperature is well to adsorption of pCNB onto MSW.

As shown in Figs. 6 and Table 1, the Frundlich isotherm is best fitted with the experimental data (R^2=0.995) and it can be conclude the Frundlich model is a suitable isotherm to describe the adsorption equilibrium of pCNB on MSW (21,22) and a multi-layer adsorption of pCNB onto MSW was occurred (23).

Competing of R^2 values (Fig. 7 and Table 2), shows that it was higher for pseudo-second-order model and adsorption of pCNB onto MSW is obeyed pseudo-second-order kinetic. In fact, adsorption rates of pCNB onto the MSW can be more appropriately described, using the pseudo-second order rate and it can be deduced that adsorption rate was twice increased by increasing of pCNB concentration.

Conclusion

Removal of pCNB, as a pollutant model by MSW by acid, is studied. Results confirmed that adsorption is depended on initial pCNB

concentration, MSW dosage and pH but independent of temperature. Maximum removal of pCNB was about 77% at 20 mg/L of pCNB concentration, pH=6, T=25°C and 5 g/ 250 ml of MSW. Also, the adsorption followed Frundlich isotherm and pseudo second-order kinetics. As results, MSW can be applied as a performance adsorbent to remove of pCNB from aqueous solutions.

Footnotes

Conflict of Interest:

The authors declared no conflict of interest.

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