FIXED-BED COLUMN BIO-SORPTION OF CONGO RED BY WATER HYACINTH STEMS FROM INDUSTRIAL EFFLUENTS

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Abstract

In present study, the ability of water hyacinths to adsorb Congo red (CR) from aqueous solutions were investigated in a fixed-bed column. Effects of important parameters, such as the value of initial pH, existed salt, the flow rate, the influent concentration of CR and bed depth, were assessed. The Thomas model was applied to adsorption of CR at different flow rate, influent concentration to predict the breakthrough curves and to determine the characteristic parameters of the column' suitability for process design using non-linear regression.

Bed-depth/service time analysis (BDST) model was also applied at different bed depths to predict the breakthrough curves. The two models were found suitable for describing the biosorption process of the dynamic behavior of the water hyacinths column.

Quoted results have suggested that water hyacinths as adsorbent to removal CR from solution be efficient, and the rate of biosorption process be rapid. When the flow rate was 0.5 ml min^{-1} and the influent concentration of CR was 30 mg l^{-1}, the equilibrium adsorption biomass reached 109 mg g^{-1} according to Thomas model.

Key words: Biosorption, fixed-bed, water hyacinth, Congo Red(CR)

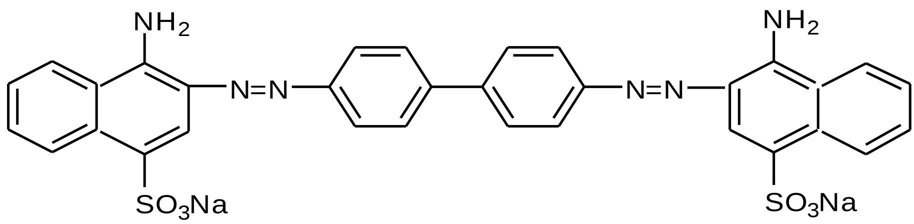
Introduction:

Many industries use dyes to color their products and also consume substantial volumes of water. Dyes are common constituents of effluents discharged by various industries, particularly the textile industry. The presence of small amounts of dyes in water is highly visible and undesirable [(1)]. Recently, an increasing interest has been focused on removing dyes from water due to its refractory biodegradation and toxic nature, which affects the aquatic biota and food web [(2)]. Adsorption technique is quite popular due to its simplicity as well as the availability of a wide range of adsorbents and it is proved to be an effective and attractive process for removal of non-biodegradable pollutants (including dyes) from wastewater [3]. The common adsorbent, activated

carbon, has good capacity of removal of pollutants [4,5]. But its main disadvantages are the high price of treatment and difficult regeneration, which increases the cost of wastewater treatment. Thus, there is a demand for other adsorbents, which are of inexpensive material and does not require any expensive additional pretreatment step. So the adsorption process will become economically viable. A successful adsorption process not only depends on dye adsorption performance of the adsorbents, but also on the constant supply of the materials for the process. So it is preferable to use low cost adsorbents, such as an industrial waste, natural ores, and agricultural byproducts. This has resulted in a search for developing other adsorbents based on solid wastes. Such low cost adsorbents have given satisfactory performance at the laboratory scale for treatment of colored effluents [6-10].

In recent years, some papers had reported several kinds of low cost adsorbents such as leaf , fly, activated carbon , red mud , waste Fe(III)/Cr(III) hydroxide and montmorillonite [11,12] for the removal of Congo red (CR) from aqueous solutions. CR containing effluents are generated from textiles, printing and dyeing, paper, rubber, plastics industries, etc. Due to its structural stability, CR is difficult to biodegrade.

In the present work, water hyacinths obtained from EL-Manzala leak was tested as an adsorbent for dyes with a model system of aqueous Congo Red solutions. Congo Red (1-naphthalenesulfonic acid, 3,3'-(4,4'-biphenylenebis(azo)) bis (4-amino-) disodium salt) is a substituted di-basic benzidine di-azo based dye of the following structure:



Direct Red 28 (C.I. 22120)

The dye is known to metabolize to benzidine, a known human carcinogen. Exposure to the dye has been known to cause an allergic reaction. The substance is considered as toxic.

The adsorption capacity parameter obtained from a batch experiment is useful in providing information about the effectiveness of dye- adsorbent system. However, the data obtained under batch conditions are generally not applicable to most treatment systems (such as column operations). Hence, there is a need to perform dynamic studies using columns.

Water hyacinths [Eichhornia Crassipes (E.C.)] (13) an aquatic plant, has spread from the American tropics and assumed a largely pan-tropical distributions and show many extreme risks. It was recorded in Egypt in the last decade of the 19th century, but it did reach the plague proportions exhibited nowadays in the Nile Delta. E.C. is the most troublesome and abundant of weeds in the River Nile and its canals. The dry matter in the standing crop weigh 50 tons/feddan. It could be one of the promising aquatic plants which may be used as a green forage during summer period and feed stuff for domestic animal. Eichhornia crassipes removed nutrients and heavy metals which was a toxic element from sewage and sludge ponds which indicate that E.C.could play a role against environmental pollution (14). Recently, utilization of E.C.in the removal of color from wastewater of textile dyeing processes was studied (15-17). Furthermore, the yield of water hyacinths obtained from Nile river is vast. Hence water hyacinths is low cost and can be easily obtained.

The aim of the present work is to explore the possibility of utilizing water hyacinth for the adsorptive removal of CR from wastewater. The effect of such factors such as the initial pH value, salt concentration, flow rate, influent concentration, mesh size of adsorbent and bed depth on CR adsorption by water hyacinth bed column was investigated. Thomas model and bed depth service time (BDST) model was used to predict the performance.

Thomas model

The data obtained in column in continuous mode studies was used to calculate maximum solid phase concentration of MB on biosorbent and the adsorption rate constant using the kinetic model developed by Thomas (18). The Thomas solution is one of the most general and widely used methods in column performance theory. The expression by Thomas for an adsorption column is given as follows:

$$\frac{Ct}{Co} = \frac{1}{1 + exp[k_{Th}\,(qox - coV_{eff})/\upsilon]} \qquad (1)$$

where k_{Th} is the Thomas rate constant (ml min^{-1} mg^{-1}), q_0 the equilibrium CR uptake per g of the adsorbent (mg g^{-1}), x the amount of adsorbent in the column (g),V_{eff} the effluent volume (ml),C_0 the influent CR concentration (mg l^{-1}), C_t the effluent concentration at time t (mg l^{-1}) and υ is the flow rate (ml min^{-1}). The value of C_t/C_0 is the ratio of effluent and influent CR concentrations. The value of time t (min) is

$$t = V_{eff}/\upsilon$$

The kinetic coefficient k_{Th} and the adsorption capacity of the column q_0 can be determined from a plot of C_t/C_0 against t at a given flow rate using non-linear regression.

The bed-depth/service time analysis (BDST) model

The BDST model is based on physically measuring the capacity of the bed at different breakthrough values. The BDST model works well and provides useful modeling equations for the changes of system parameters [19]. A modified form of the equation that expresses the service time at breakthrough, t, as a fixed function of operation parameters is BDST model :

$$t = \frac{N_o}{C_oF} Z - \frac{1}{K_aC_o} \ln\left(\frac{C_o}{C_t} - 1\right) \qquad (2)$$

where C_t is the effluent concentration of solute in the liquid phase (mg l^{-1}),C_0 the initial concentration of solute in the liquid phase (mg l^{-1}), F the influent linear velocity (cm min^{-1}), N_0 the adsorption capacity (mg g^{-1}), K_a the rate constant in BDST model (l mg^{-1} min^{-1}), t the time (min) and Z is the bed depth of column (cm).

A plot of t versus bed depth, Z, should yield a straight line where N_0 and K, the adsorption capacity and rate constant, respectively, can be evaluated.

A simplified form of the BDST model is :

$$t = aZ - b \qquad (3)$$

Where :

$$a = \frac{N_o}{C_o F}, \quad b = \frac{1}{K_a C_o} \ln\left(\frac{C_o}{C_t} - 1\right) \qquad (4)$$

The slope constant for a different flow rate can be directly calculated by Eq. (5) [20]:

$$a' = a\,\frac{F}{F'} = a\,\frac{\upsilon}{\upsilon'} \qquad (5)$$

where a and F are the old slope and influent linear velocity, respectively, and a' and F' are the new slope and influent linear velocity. As the column used in experiment has the same diameter, the ratio of original (F) and the new influent linear velocity (F') and original flow rate (υ) and the new flow rate (υ') is equal.

For other influent concentrations, the desired equation is

given by a new slope, and a new intercept given by:

$$a' = a\,\frac{C_o}{C'_o} \qquad (6)$$

$$b' = b\,\frac{C_o}{C'_o}\,\frac{\ln(C'_o - 1)}{\ln(C_o - 1)} \qquad (7)$$

where b', b are the new and old intercept, respectively, C'_0 and C_0 are the new and old influent concentration, respectively.

Experimental:

Preparation of water hyacinth

Fresh biomasses of water hyacinth were collected from El-Manzala Lake, north Egypt, during the summer season in 2008.The samples were thoroughly washed with tap water, the Stems were cut out from the plant, cut to chips and then air dried. The dry biomass material was sieved and a fraction of 30-40 mesh washed with distilled water after time to remove water soluble compounds then dried in oven at 60 degree centigrade and used directly for column studies.

CR solution

The stock solutions of CR (500 mg l^{-1}) were prepared in distilled water. All working solutions were prepared by diluting the stock solution to the needed concentration.

Methods of adsorption studies

Continuous flow biosorption experiments were conducted in a glass column (1 cm internal diameter and 25 cm height). A series of experiments were conducted with various influent water and water hyacinth columns. The temperatures of all experiments at room temperature. Water hyacinth was packed into a glass column. The mass of water hyacinth in the column was 0.5 g (10 cm) and the value of pH was near 4. The pH of CR solution was adjusted by adding 0.1 mol l^{-1} hydrochloric acid or NaOH solution. No other solution was provided in the experiment. The CR solution of known concentration was pumped to the column in a down-flow direction by a dozing pump at a certain rate. Samples were collected at regular intervals in all the adsorptions. The concentration of CR in the effluent was analyzed using a UV/Vis- spectrophotometer (Perkin elemer, lambda 35 UV/vis spectrometer) by monitoring the absorbance changes at a wavelength of maximum absorbance (497 nm).Calibration curves were plotted between absorbance and concentration of the dye solution. Also, the experiments of three different bed depths, 10 cm (0.5 g),15 cm (0.75 g),and 20 cm (1.0 g),were operated at the same influent CR concentration (20 mg l^{-1}) and flow rate (1ml min-1), respectively.

:Results and discussion

Effect of the initial solution pH on the breakthrough curve

In order to examine the effect of initial pH value on biosorption in columns, CR adsorption experiments were done at pH of 4.0, 7.0 and 9.0. Fig.1. showed the breakthrough curve using a plot of dimensionless concentration (C_t/C_o) Versus time (t) at pH values of 4.0, 7.0 and 9.0. As shown in Fig. 1. ,with an increase of pH in the influent, the breakthrough curves shifted from right to left, which indicated that less CR was removed. It would require less time to reach the saturation, and the efficiency of biosorption was much lower. The results suggested that with the increasing of pH in the experimental condition, the adsorption capacities decrease. So the removal of CR from aqueous solution was more efficient at lower initial pH value. Several reasons may be attributed to CR adsorption behavior of the adsorbent relative to solution pH.The surface of water hyacinth may contain a large number of active sites and CR uptake can be related to the active sites and also to the chemistry of the solute in the solution. Two possible mechanisms of CR adsorption on adsorbents may be considered:(a) electrostatic interaction between the protonated groups of carbon and acidic dye and (b) the chemical reaction between the adsorbate and the adsorbent [11].

CR is a relatively large molecule and negatively charged for much of the pH range (>5) .At pH 4.0, a significantly high electrostatic attraction exists between the positively charged surface of the adsorbent and anionic dye. A negatively charged surface site on the Rice husk does not favor the adsorption of dye anions due to the electrostatic repulsion. Also, there was competition between OH^- (at higher pH) and colored ions of CR for positively charged adsorption sites [21].

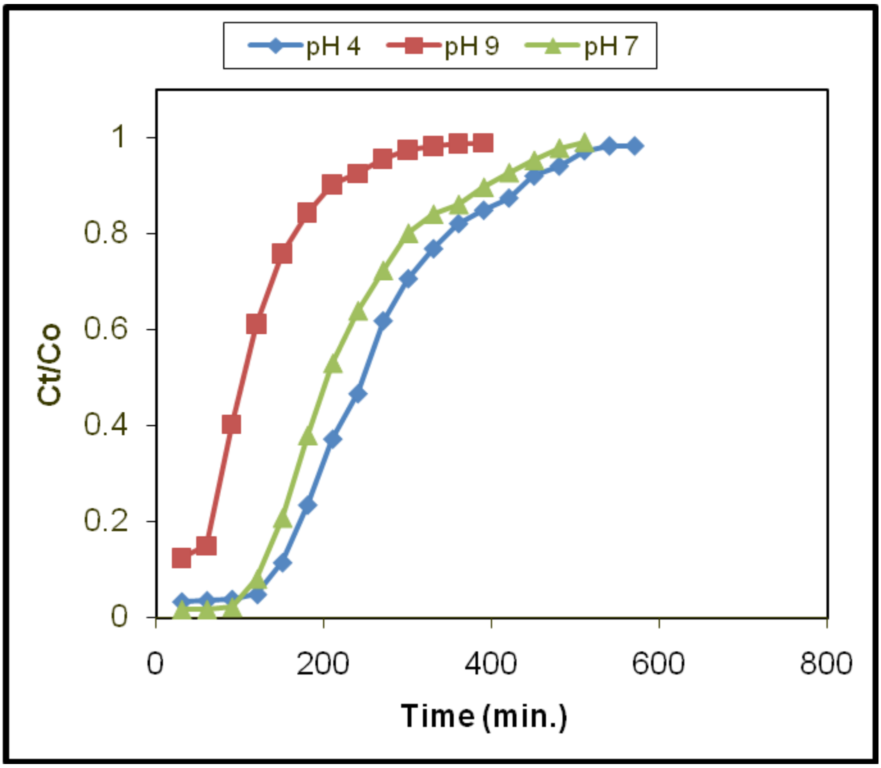


Fig. 1. Breakthrough curves of the effects of pH values on biosorption of CR onto water hyacinth (F = 1 ml min^{-1}, C_o = 20 mg l^{-1})

The effect of flow rate on breakthrough curve

The breakthrough curves at various flow rates were shown in Fig. 2. It was seen from Fig. 2. that breakthrough curves generally occurred faster with higher flow rate. Breakthrough time for reaching saturation was increased significantly with a decrease in the flow rate. When at a lower rate of influent, CR had more time to contact with water hyacinth stems and resulted in higher removal of CR in the column. The variation in the slope of the breakthrough curve and adsorption capacity may be explained on the basis of mass transfer fundamentals. The reason is that at higher flow rate, the rate of mass transfer tends to increase. The amount of dye adsorbed onto the unit bed height (mass transfer zone) increased with increasing flow rate leading to faster saturation at a higher flow rate [22].

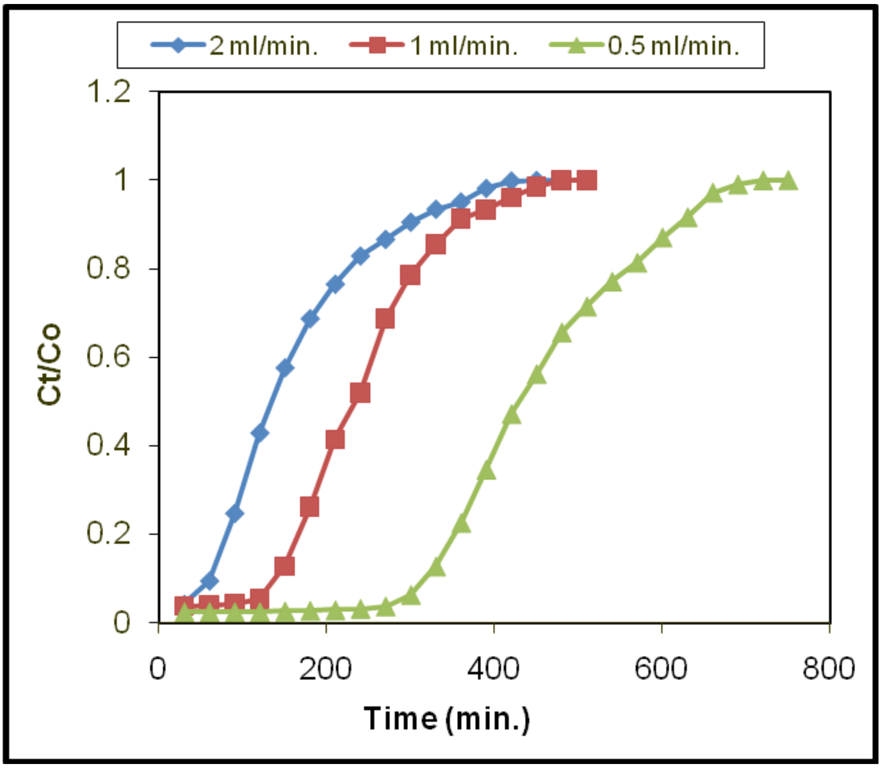


Fig. 2. Breakthrough curves of the effects of flow rates on biosorption of CR onto water hyacinth (F = 1 ml min^{-1}, C_o = 20 mg l^{-1})

The effect of different bed depth on the breakthrough curve

The breakthrough curves at different bed depths were shown in Fig. 3. From Fig. 3., it was seen that as the bed height increased, CR had more time to contact with the water hyacinth stems that resulted in higher removal efficiency of CR. So the higher bed column resulted in a decrease in the solute concentration in the effluent at the same time. The slope of breakthrough curve decreased with increasing bed height, which resulted in a broadened mass transfer zone. Higher uptake was observed at the highest bed height due to an increase in the surface area of the biosorbent, which provided more binding sites for the sorption[23].

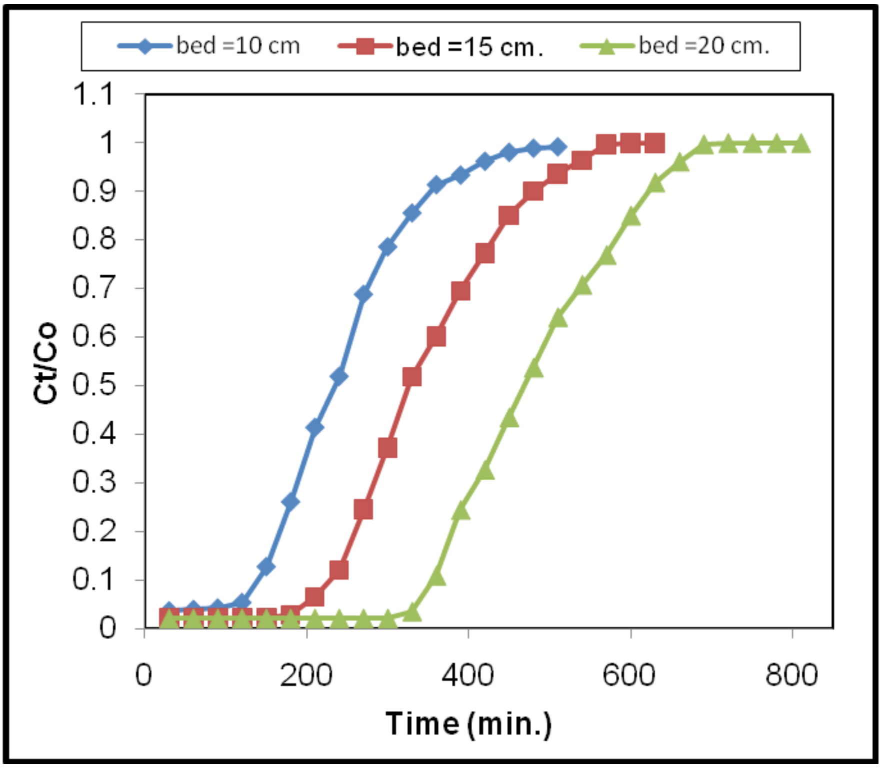


Fig. 3. Breakthrough curves of the effects of different bed depth on biosorption of CR onto water hyacinth (F = 1 ml min^{-1}, C_o = 20 mg l^{-1})

The effect of initial concentration on breakthrough curve

The breakthrough curves at various initial concentrations were shown in Fig. 4. It was seen from Fig. 4. that the breakthrough time decreased with increasing influent CR concentration. At lower influent CR concentrations, breakthrough curves were dispersed and breakthrough occurred slower. As influent concentration increased, sharper breakthrough curves were obtained. These results demonstrated that the change of concentration gradient affected the saturation rate and breakthrough time .This can be explained by the fact that more adsorption sites are being covered with the increase in CR concentration. The larger the influent concentration, the steeper the slope of the breakthrough curve and smaller the breakthrough time. These results demonstrated that the change of concentration gradient affected the saturation rate and breakthrough time, or in other words, the diffusion process was concentration dependent. As the influent concentration increases, CR loading rate increases, so does the driving force for mass transfer, which results in a decrease in the adsorption zone length [24].

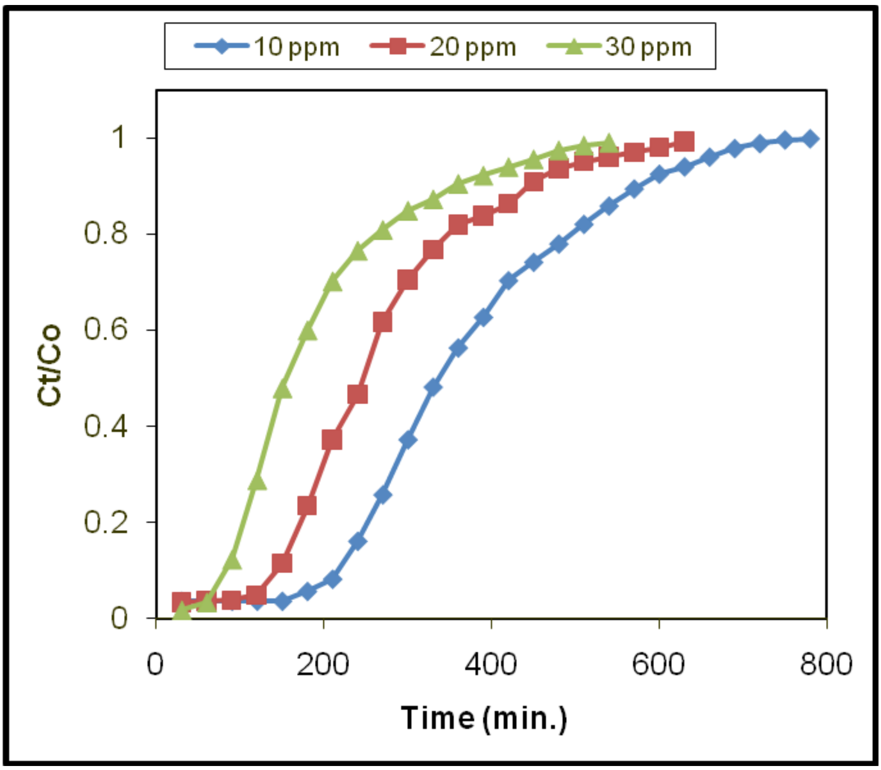


Fig. 4. Breakthrough curves of the effects of different conc. on biosorption of CR onto water hyacinth (F = 1 ml min^{-1}, C_o = 20 mg l^{-1})

The effect of NaCl existing in solution on breakthrough curve

Fig. 5. showed the breakthrough curves when, NaCl existed as well as when it does not exist in solution. As shown in Fig. 5., the existence of salt in solution resulted in the breakthrough curve from right to left and with higher CR removal capacity. The electrolytes in solution reduced repulsive forces between the dye and the functional groups in the surface of the water hyacinth due to screening effect of the superficial charge. When 0.1 mol $^{-1}$ of NaCl existed in the solution, it was possible to decrease the repulsive forces and thus increase the anionic exchange capacity. So water hyacinth can be used to remove CR from aqueous solution with a higher salt concentration.

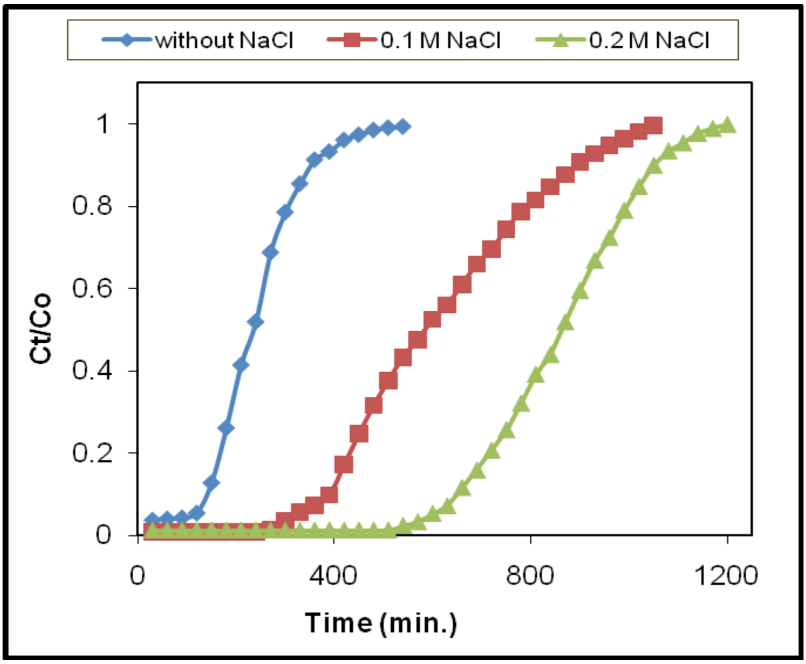


Fig. 5. Breakthrough curves of the effects of existing salt (NaCl) on biosorption of CR onto water hyacinth (F = 1 ml min^{-1}, C_o = 20 mg l^{-1})

Estimation of breakthrough curves

In order to describe the fixed-bed column behavior and to scale it up for industrial applications, tow models, Thomas and BDST were used to fit the experimental data in the column.

Modeling of different bed depth column study results about: BDST model

The lines of t–Z at values of C_t/C_0 0.2, 0.4 and 0.6 were shown in Fig. 6., respectively. The related constants of BDST according the slopes and intercepts of lines are listed in Table 1.

From Table 1, as the value of C_t/C_0 increased, the rate constant of K_a decreased while the adsorption capacity of the bed per unit bed volume, N_0, increased. From the values of R^2 , it indicated the validity of BDST model for the present system. The BDST model constants can be helpful to scale up the process for other flow rates and concentration without further experimental run. The BDST equation obtained at flow rate 1 ml min^{-1} and influent concentration 20 mg l^{-1} was used to predict the adsorbent performance at lower flow rates of 0.5 ml min^{-1} and lower influent concentration of 10 mg l^{-1}, respectively. From Tables 2 and 3, good prediction has been found for the case of changed feed concentration and flow rate. Thus, model and the constants evaluated can be used to design columns over a range of feasible flow rates and concentrations at C_t/C_0 = 0.2, 0.4 and 0.6, respectively.

These results indicate that the equation can be used to predict adsorption performance at other operating conditions for adsorption of CR onto WHS.

Table 1: The calculated constants of BDST model for the adsorption of CR (C_o = 20 mg^{-1}, F = 1 ml min^{-1})

C_t/C_o	a (min cm^{-1})	b (min)	K_a ($lmg^{-1}min^{-1}$)	N_o (mg l^{-1})	R^2
0.2	21	-35	0.00202	420	0.993
0.4	24	-10	0.00198	480	0.979
0.6	27	-5	-0.00405	540	0.995

Table 2: Predicted breakthrough time based on the BDST constants for a new flow rate (C_o = 20 mg l^{-1})

C_t/C_o	a (min cm^{-1})	b (min)	F (ml min^{-1})	F'	a'	Z (cm)

0.2	21	-35	1	0.5	42	10
0.4	24	-10	1	0.5	48	10
0.6	27	-5	1	0.5	54	10

Table 3: Predicted breakthrough time based on the BDST constants for a new influent concentration (F = 1ml min^{-1})

C_t/C_o	a (min cm^{-1})	b (min)	C_o (mg l^{-1})	C'_o	a'	b'	Z (cm)
0.2	21	35	20	10	42	52.32	10
0.4	24	10	20	10	48	15	10
0.6	27	5	20	10	54	7.5	10

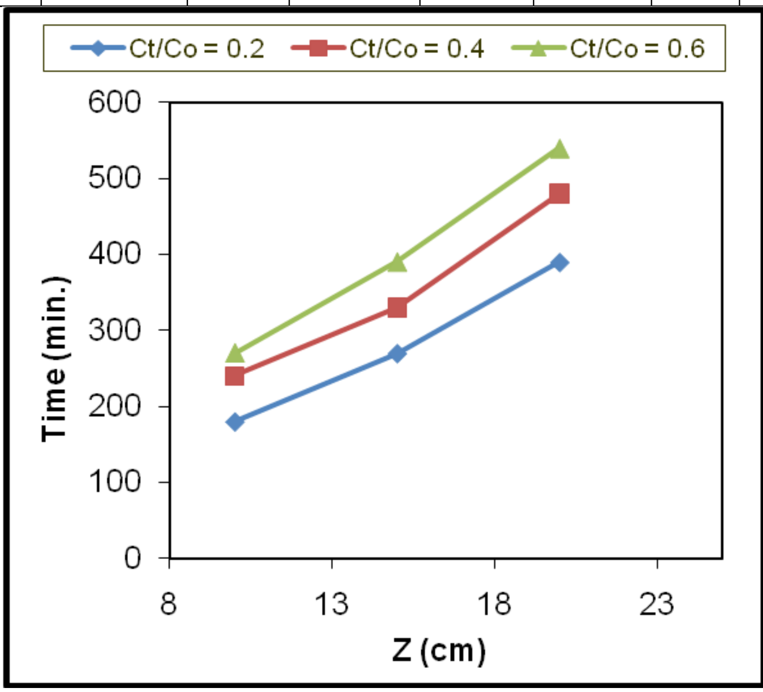


Fig. 7. Isoremoval lines for 0.2,0.4,0.6 breakthrough for different bed height (C_o = 20 mg l^{-1} , F = 1ml min^{-1})

Modeling of column study results: Thomas model

Thomas model was applied to the experimental data with respect to flow rate, influent concentration of CR and bed depth.

A non-linear regression analysis was used on each set of data to determine the Thomas model parameters of q_0 and k_{Th}. The determined coefficients is also obtained using nonlinear regression analysis according Eq. (1). The results were listed in Table 4. They were all fits with higher determined coefficients (R^2) ranging from 0.866 to 0.969.

As shown in Table 4, as the influent concentration increased, the value of q_0 increased but the value of k_{Th} decreased. The reason is that the driving force for biosorption is the concentration difference between the dye on the biosorbent and the dye in the solution (25-27) . Thus the high driving force due to the higher CR concentration resulted in better column performance. With flow rate increasing, the value of q_0 decreased but the value of k_{Th} increased. So higher flow rate and lower influent concentration have disadvantage to adsorption of CR on water hyacinths steam.

Table 4: calculated constants of Thomas models at different conditions using non-linear regression analysis

C_o (mg l^{-1})	υ (ml min^{-1})	Z (cm)	k_{Th} (x 10^{4-}) (mlmin^{-1}mg^{-1})	q_0 (mg g^{-1})	R^2
30	1	10	-3.3	109	0.912
20	1	10	-3.6	77.7	0.969
10	1	10	- 5.8	41.3	0.962
20	0.5	10	-3.2	84.37	0.949
20	2	10	-2.2	18.18	0.866

Conclusions:

On the basis of the experimental results of this investigation, the following conclusion can be drawn:

a. Water hyacinths stem as adsorbent can be used to removal CR

from solution.

b. The biosorption of CR was dependent on the flow rate, the inlet CR concentration and bed depth.

c. The initial region of breakthrough curve was defined by the Adams–Bohart model at all experimental condition studied while the full description of breakthrough could be accomplished by Thomas models.

d. BDST model adequately described the adsorption of CR onto Water hyacinths stems by column mode.

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