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Equilibrium, kinetic and mechanism study for the adsorption of neutral red onto rice husk

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ABSTRACT

Adsorption of neutral red (NR) onto rice husk from aqueous solutions was investigated. Experiments were carried out as a function of pH, adsorbent dosage, contact time and dye concentration. The equilibrium adsorption data were analyzed by Langmuir, Freundlich, Redlich–Peterson models using nonlinear regressive analysis. The results indicated that the Langmuir and Redlich–Peterson models provided the best correlation of the experimental data. The adsorption capacities of NR adsorption onto rice husk from Langmuir model were 25.16, 29.15, 32.37 mg/g at 288, 308, 318 K, respectively. Adsorption kinetic data were fitted using the pseudo-first-order kinetic model and pseudo-second-order kinetics. It was shown that the pseudo-first-order and second-order kinetic equations could describe the adsorption kinetics. The process mechanism was found to be complex, consisting of both surface adsorption and pore diffusion. The effective diffusion parameter D_i values estimated in the order of 10^{-9} cm^2/s indicated that the intraparticle diffusion was not the rate-controlling step. Using the equilibrium concentration constants obtained at different temperatures, various thermodynamic parameters, such as ΔG^0, ΔH^0 and ΔS^0, have been calculated. The thermodynamics parameters of NR/rice husk system indicated spontaneous and endothermic process. It was implied that rice husk may be suitable as adsorbent material for adsorption of NR from aqueous solutions.

Keywords: Rice husk; Neutral red; Adsorption isotherms; Kinetics; Thermodynamics

1. 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 industries. Dyeing wastewater discharged to natural receiving waters may make them unacceptable for public consumption. The presence of small amounts of dyes in water is highly visible and undesirable [1,2]. Thus, it is desirable to eliminate dyes from textile wastewater [3].

Adsorption technique is quite popular due to its simplicity as well as the availability of a wide range of adsorbents [3–5]. It is proved to be an effective and attractive process for removal of non-biodegradable pollutants (including dyes) from wastewater. Currently, the most widely used and effective physical method in industry is activated carbon and it can be regenerated by thermal desorption or combustion of the toxicant in air, but it is still considered expensive [1,2].

Thus, there is a demand for other adsorbents, which are of inexpensive material and do not require any expensive additional pretreatment steps. So the adsorption process will become economically viable. In recent years,

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agricultural by-products, such as peanut husk [6], peat and pith [7], apple pomace and wheat straw [8], wheat shell [9], cereal chaff [10], fruit peel [11], de-oil soya [12] and leaves [13] have been widely studied for dyes removal from wastewater.

One potential adsorbent material can be rice husk, which can be utilized for such purposes as it can also bring unlimited number of economic and environmental benefits to the industrial wastewater treatment. Rice husk is a by-product during rice-milling process which is extensively cultured in many countries. Rice husk contains abundant floristic fiber, protein and some functional groups such as carboxyl, hydroxy and amidogen etc, which make adsorption processes possible [14]. Furthermore, the yield of rice husk obtained from agriculture as a byproduct is vastness. So the rice husk is low cost and easy to obtain. Rice husk has been used to adsorb several dyes [15,16]. Up to the best of our knowledge, there is no paper dealing with the adsorption of neutral red (NR) on rice husk.

The objective of this study is to evaluate the adsorption potential of rice husk for NR removal. The effects of various factors on adsorption such as pH, adsorbent dosage, contact time, temperature and initial dye concentration are studied. The equilibrium and kinetic data of adsorption studies are processed to understand the adsorption mechanism of NR onto rice husk.

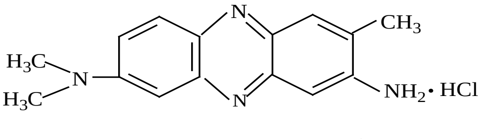
2. Materials and methods

2.1. Preparation of rice husk

Fresh biomass of rice husk was collected from its natural habitats on the dead millet in the farmland, Zhengzhou City, China. It was washed a few times with distilled water, dried for 8 h at 60°C in the oven. The biomass was sieved and a fraction of 40–60 mesh was used for adsorption studies.

2.2. Preparation of NR solutions

NR (C.I.50040, FW = 288.8) was purchased from Zhengzhou Chemical Company, China. The formula is as follows:



The stock solutions of NR (500 mg/L) were prepared in distilled water. All working solutions were prepared by diluting the stock solution with distilled water to the needed concentration.

2.3. Experimental method

In this study 10 ml of dye solution of known initial dye concentration was agitated with weighed amount of rice husk in 50 ml capped conical flasks for 8 h, which was more than sufficient to reach equilibrium, except the effect of contact time on adsorption. The contact was made using a water bath shaker at a constant temperature and at a constant agitation speed of 100 rpm. As NR is precipitated when pH is over 7 in an experiment, the effect of pH on the amount of color removal was analyzed over the pH range from 1 to 7. The pH was adjusted using 1 mol/L NaOH or HCl solutions.

Kinetic experiments were carried out as follows: weighed amount of rice husk was loaded into the several sets of conical flasks containing 10 ml of dye solution of known initial concentration. The flasks were then subjected to agitation using water bath shakers for different contact time intervals. Flasks were taken from the shakers at regular time intervals and the left out concentration of dye in the solution was estimated.

After adsorption, the rice husk was separated by filtration (carried out using paper filter) and the remaining dye concentration was analyzed using a UV/Vis-3000 spectrophotometer (Shimadzu Brand UV-3000) by monitoring the absorbance changes at a wavelength of maximum absorbance (530 nm). Calibration curves were plotted between absorbance and concentration of the dye solution. The amount of dye adsorbed onto unit weight of adsorbent (q) and percent color removal were calculated using the following equations, respectively:

$$q = \frac{V(c_0 - c)}{m} \tag{1}$$

$$\%\,\text{removal} = \frac{c_0 - c}{c_0} \tag{2}$$

where V is the solution volume in L, c_0 is the initial NR concentration in mg/L, c is the NR concentration at any time t in mg/L, and m is the dry weight of rice husk in g.

3. Results and discussion

3.1. Effect of initial pH

Initial pH value of solution is one of the most important factors influencing the dye adsorption. Fig. 1 shows the effect of pH on adsorption capacity of NR on rice husk at different initial solution pH for the dye concentration of 80 mg/L and at 288 K. As seen in Fig. 1, maximum color removal was observed at pH 5–7. For this reason, the solution was not adjusted in the other experiments as the initial pH of NR solution near 6.5.

Basic dye was dissolved and released colored dye cation in the solution. The adsorption of these charged dye groups onto the adsorbent surface was primarily influenced by the surface charge on the adsorbent which in turn was influenced by pH of the solution. Several reasons may be attributed to dye adsorption behavior of the adsorbent relative to solution pH. The surface of rice

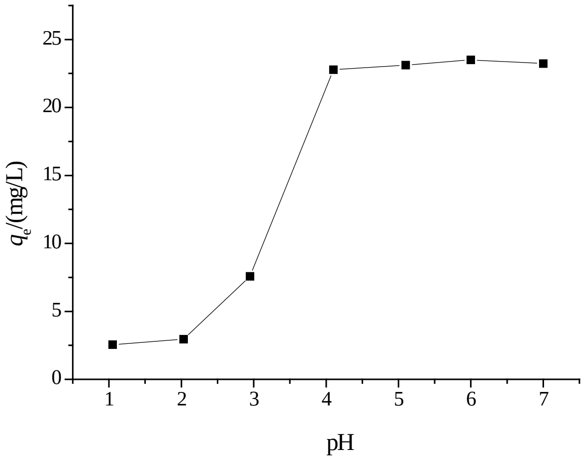


Fig. 1. The effect of initial pH on adsorption (Initial NR concentration 80 mg/L, rice husk dosage 3 g/L).

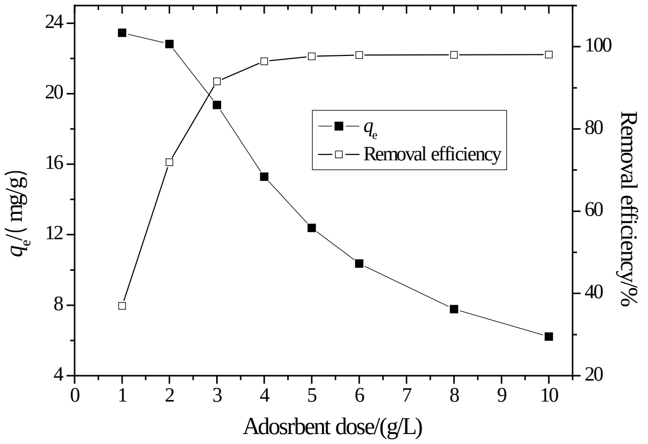


Fig. 2. Effect of rice husk dosage on the removal of NR (Initial NR concentration 60 mg/L).

husk may contain a large number of active sites and the dye ions uptake can be related to the active sites and also to the chemistry of the solute in the solution. At lower pH, the surface charge of adsorbent may get positively charged, thus making H^+ ions compete effectively with positive dye cations, then results in a decrease in the amount of dye adsorbed (mg/g). At higher pH, the surface of adsorbent particles may get negatively charged. NR, as a basic dye, will produce cations in water. The association of dye cations on solid will take place more easily when the pH of the dye solution becomes higher. The structure of rice husk is cellulose based, and the surface of cellulose in contact with water is negatively charged. Dissolved NR are positively charged and will undergo attraction on approaching the anionic rice husk structure. On this basis, it is expected that a NR will have a strong sorption affinity for adsorbent.

3.2. *Effect of adsorbent dose*

The amount of adsorption and percentage removal of NR at different doses of adsorbent is shown in Fig. 2.

It is observed from Fig. 2 that the amount of dye adsorbed was varied with varying the adsorbent mass and values of q_e decreased with increasing the adsorbent mass. In other words, the value of q_e got decreased with the increase in biomass concentration. The NR uptake decreased from 23.45 mg/g to 6.22 mg/g for an increase in biomass concentration from 1 g/L to 10 g/L. But the percent removal of NR increases from 36.97 % to 98.05 % for an increase in the adsorbent dose from 1 g/L to 10 g/L. It is apparent that by increasing the dose of the rice husk, the number of sorption sites available for sorbent–solute interaction is increased, thereby resulting in the increased percentage dye removal from the solution.

The primary factor explaining the decrease in q_e (mg/g) value is due to the split in the concentration gradient between solute concentration in the solution and the solute concentration on the surface of the adsorbent. Thus with increasing the adsorbent mass, the amount of dye adsorbed onto unit weight of the adsorbent gets reduced, thus causing a decrease in q_e value with increasing the adsorbent mass concentration [15]. Another reason may be attributed to overlapping or aggregation of the adsorbent surface area available to NR adsorption and an increase in diffusion path length. Similar results were reported previously [10,17,18].

3.3. *Effect of NaCl and $CaCl_2$ concentration on adsorption*

The wastewater containing dye has commonly higher salt concentration, and effects of ionic strength are of some importance in the study of dye adsorption onto adsorbents. Fig. 3 shows the effect of various concentrations of NaCl and $CaCl_2$ solution on the values of q_e and p for an initial NR concentration of 100 mg/L and rice husk dose of 3 g/L.

From Fig. 3, the presence of NaCl and $CaCl_2$ in the solution affected the NR adsorption onto the rice husk. It is seen that the increase in the salt concentration resulted in a decrease of values of q_e and percent removal efficiency (p). This trend indicated that the adsorbing efficiency decreased when NaCl and $CaCl_2$ concentration increased in the NR solution, which could be attributed to the competitive effect between NR ions and cations from the salt for the sites available for the adsorption process. As Ca^{2+} has more contribution to ionic strength and more positive charge than Na^+, the effect of Ca^{2+} on adsorption is more serious than Na^+ in the same mole concentration [10].

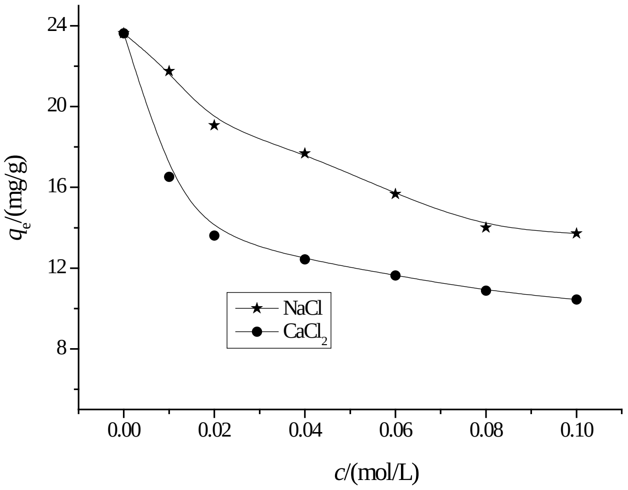


Fig. 3. The effect of NaCl and $CaCl_2$ concentration on adsorption and percent removal efficiency (c_0 = 100 mg/L, rice husk dose = 3 g/L).

3.4. The effect of equilibrium NR concentration on temperature-dependent adsorption

The effect of initial dye concentration on the NR adsorption by rice husk was investigated in the range of 10–200 mg/L. Fig. 4 shows the equilibrium quantity at different initial dye concentration.

From Fig. 4, the values of q_e increased with increasing c_e. The initial concentration provided the necessary driving force to overcome the resistances to the mass transfer of NR between the aqueous and solid phases. The increase in c_e also enhanced the interaction between NR and rice husk. Therefore, an increase in c_e of NR enhanced the adsorption uptake of NR.

The bigger adsorptive capacity of NR was also observed in the higher temperature range. This was due to the increasing tendency of adsorbate ions to adsorb from the solution to the interface with increasing temperature. The increase of the equilibrium adsorption with increased temperature indicated that the adsorption of NR ions onto rice husk is endothermic in nature.

3.5. The effect of contact time on adsorption at various initial NR concentrations

The rate of NR adsorption on rice husk was determined as a function of the initial NR concentrations. The uptake of NR for three initial NR concentrations at different contact time is listed in Fig. 5.

The results showed that the adsorption of NR onto rice husk increased with increasing the contact time at different conditions. Kinetics of adsorption of NR consisted of two phases: an initial rapid phase where adsorption was fast and contributed significant to equilibrium uptake and a slower second phase whose contribution to the total NR adsorption was relatively small. It was also seen that equilibrium time occurred relatively earlier in the solution containing lower NR concentrations. The necessary time to reach equilibrium was variable according to the initial concentration. From Fig. 4, the equilibrium time is to 180, 270, 300 min with the initial NR concentration of 60, 80, 100 mg/L, respectively. Furthermore, the value of q_e is 18.60, 23.69, 25.69 mg/g with three levels of concentration, respectively. So the adsorptive capacity of rice husk at equilibrium increased with the initial concentration increasing. This was obvious because more efficient utilization of the adsorption capacities of the adsorbent was expected due to a greater driving force by a higher concentration gradient pressure.

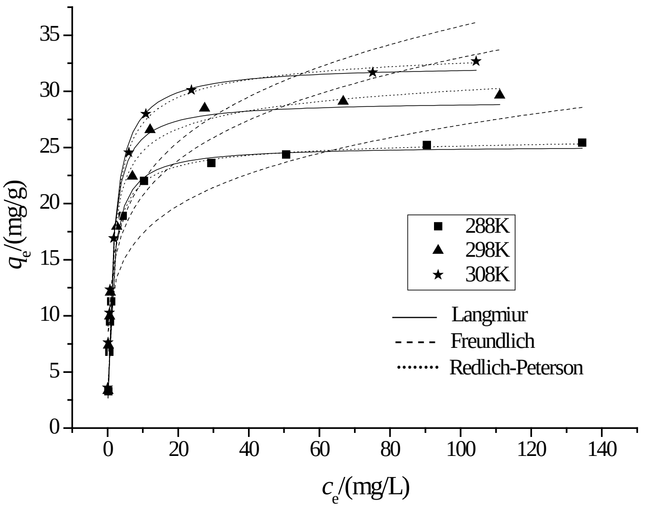


Fig. 4. Equilibrium adsorption quantities of NR adsorption at different equilibrium NR concentration and predicted isotherm curves (rice husk dose = 3 g/L).

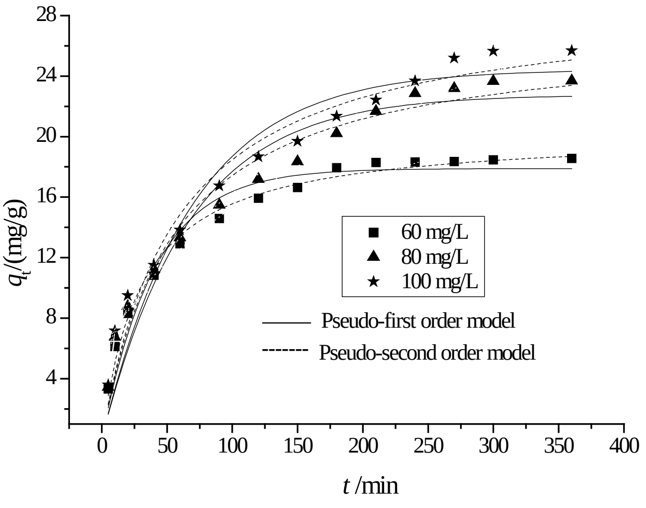


Fig. 5. Effect of contact time on NR adsorption at various initial concentrations (288 K, rice husk dose = 3 g/L).

3.6. Adsorption isotherms of adsorption

The design and efficient operation of adsorption processes require equilibrium adsorption data. The equilibrium isotherm model plays an important role in predictive results for analysis and design of adsorption systems [20,21].

Various isotherm equations have been used to describe the isotherm curve. The relative parameters of each equation are obtained using least square sum (SS) between the calculated data and experimental data by nonlinear regressive analysis. The calculated expression of SS is as follows:

$$\mathrm{SS} = \sum (q_c - q_e)^2 \tag{3}$$

where q_c is the predicted (calculated) quantity of NR adsorbed onto rice husk according to adsorption models and q_e is the experimental data.

In the present study the Langmiur, Freundlich and Reclich-Peterson isotherm models were used to describe the adsorption equilibrium. The equations are presented in Table 1.

Table 1
Equations of Langmiur, Freundlich and Reclich–Peterson isotherm model

Isotherm	Equation	Ref.
Langmuir	$q_e = \dfrac{q_m K_L c_e}{1 + K_L c_e}$	[22]
Freundlich	$q_e = K_F c_e^{1/n}$	[23]
Redlich–Peterson	$q_e = \dfrac{A c_e}{1 + B c_e^g}$	[24]

Note: qm is the qe for a complete monolayer (mg/g) and K_L is a constant related to the affinity of the binding sites and energy of adsorption (L/mg); K_F and $1/n$ are the Freundlich constants; A, B and g are the Redlich–Peterson parameters, respectively.

The isotherm constants, their correlation coefficients and values of SS are listed in Table 2.

All relative parameters of isotherm equation and determined coefficients (R^2), values of SS are listed in Table 2, respectively. Fig. 4 also shows the experimental equilibrium data and fitted equilibrium curve by three various isotherms at different temperature, respectively.

From Table 2, the adsorption capacity of rice husk (q_m) increased on increasing the temperature. The values of q_m obtained at 288 K, 308 K, 318 K are 25.16, 29.15, 32.37 mg/g, respectively.

Examination of the data showed that the Redlich–Peterson isotherm is an appropriate description of the data for NR adsorption over the concentration ranges studied. The constant g is near to 1, and these indicate the isotherm is approaching the Langmuir form.

Based on the values of R^2, SS, and from Fig. 4, the nonlinear forms of the Langmuir, Redlich–Peterson isotherms appear to produce a better model for adsorption in NR/rice husk systems, while the nonlinear form of the Freundlich isotherm appears to produce a reasonable model at three different temperatures.

It is also observed from Table 2 that the values of R^2 about Freundlich were lower and those of SS were larger. The fitted curves from Freundlich model in Fig. 4 were not consistent with the experimental curves, so Freundlich model was not suitable to fit the equilibrium data.

Table 2
Isotherm constants for NR adsorption onto rice husk

T (K)	288	308	318
Langmuir			
K_L (L/mg)	0.767±0.041	0.775±0.095	0.608±0.135
q_m (mg/g)	25.16±0.26	29.15±0.72	32.37±1.62
R^2	0.997	0.984	0.980
SS	0.228	1.97	2.88
Freundlich			
K_F	11.17±1.43	13.03±1.46	13.55±1.80
$1/n$	0.192±0.034	0.202±0.032	0.211±0.037
R^2	0.857	0.879	0.843
SS	11.60	13.37	20.90
Redlich–Peterson			
A	20.614±1.67	29.11±3.99	21.74±6.70
B	0.877±0.085	1.22±0.24	0.745±0.374
g	0.983±0.010	0.948±0.019	0.973±0.058
R^2	0.998	0.992	0.983
SS	0.224	1.04	2.76

3.7. Kinetics model of adsorption

In order to analyze the adsorption kinetics for the adsorption of NR, the pseudo-first-order kinetic model, pseudo-second-order kinetic model and intraparticle diffusion model were applied.

The pseudo-first-order kinetic model [25,26]:

$$q_t = q_e (1 - e^{-k_1 t}) \tag{4}$$

The pseudo-second-order kinetic model [26]:

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

where q_e and q_t are the amount of NR adsorbed per unit weight of the adsorbent at equilibrium and at any time t, respectively (mg/g) and k_1 is the rate constant of pseudo-first-order adsorption (1/min); k_2 is the rate constant of pseudo-second-order adsorption (g/(mg min)).

The values of q_e, k_1 and k_2 can be determined using nonlinear regressive analysis according to experimental data. The parameters are listed in Table 3. The fitted curves are also shown in Fig. 5.

From Table 3, the values of R^2 (greater than 0.98) and SS (less than 4) were only slightly different in pseudo-first-order equation and pseudo-second-order equation, respectively. The calculated values of q_e obtained from pseudo-first-order model and pseudo-second-order model agree better with the experimental $q_{e(exp)}$ values at different initial NR concentrations, so it was concluded that both models can predict the kinetic process in experimental conditions. But from values of R^2 and SS, pseudo-second-order kinetic model is better to fit the whole adsorption process. Pseudo-second-order kinetics assumes that the adsorption is chemisorption [19]. Thus it can be concluded that NR adsorption onto rice husk is chemical adsorption.

3.8. Mechanism of adsorption

For practical applications of adsorption such as process design and control, it is important to understand the dynamic behavior of the system. Webber's pore-diffusion model (intraparticle diffusion model) [27] and Boyd's equation [28] are the two most widely used models for studying the mechanism of adsorption.

The intraparticle diffusion model [27]:

$$q_t = kt^{1/2} + C \tag{6}$$

k is the intraparticle diffusion rate constant (g/(mg min$^{1/2}$), C is a constant that gives idea about the thickness of the boundary layer.

It can be seen from Eq. (9) that if pore diffusion is the rate limiting step, a plot of q against $t^{0.5}$ must give a straight line with a slope that equals k_i and the intercept value, c represents the resistance to mass transfer in the external liquid film. Fig. 6 shows the pore diffusion plot of NR adsorption on rice husk at 288 K. It is clear that the plots are two-linear, containing at least two linear segments. The regression results are presented in Table 4. For all the two-linear plots in Fig. 6, the regression estimates of the first linear segments had intercept values different from zero suggesting that pore diffusion be not the step controlling the overall rate of mass transfer at the beginning of batch adsorption. Film-diffusion control may have taken place and ended in the early stages of adsorption, or maybe it is still controlling the rate of mass transfer in the time period of the first linear segment.

This shows that the mechanism of NR adsorption on rice husk is complex and both the surface adsorption and intraparticle diffusion contribute to the actual adsorption process. It is also observed in Table 4 that an increase in the initial NR concentration increases the pore diffusion rate parameters. The increase in NR concentration results in the increase of the driving force, which increases the diffusion rate of the molecular dye in pores.

Due to the double nature of intraparticle diffusion (both film and pore diffusion) (Fig. 6), and in order to determine the actual rate-controlling step involved in the NR adsorption process, the kinetic data were further analyzed using the kinetic expression given by Boyd et al. [28]:

$$F = 1 - \frac{6}{\pi^2}\exp(-Bt) \tag{7}$$

where B is a constant and F is the fractional attainment of equilibrium at time t given by

$$F = \frac{q_t}{q_e} \tag{8}$$

where q_e and q_t represent the amount of NR adsorbed (mg/g) at equilibrium and any time t, respectively. To

Table 3
Kinetic parameters for the adsorption of NR using nonlinear regressive analysis

c_0 (mg/L)	60	80	100
Pseudo-first- order kinetic			
k_1 (l/min)	0.0247±0.0026	0.0150±0.0022	0.145±0.0021
q_e (mg/g)	17.89±0.42	22.77±0.92	24.44±1.02
R^2	0.958	0.934	0.934
$q_{e\text{-exp}}$ (mg/g)	19.02	24.32	26.5
SS	1.19	3.27	3.81
Pseudo-second –order kinetic			
k_2 (g/mg min)	0.00163±0.00015	0.00068±0.00013	0.00059±0.00011
q_e (mg/g)	20.27±0.34	26.92±0.12	29.26±1.236
R^2	0.990	0.968	0.969
SS	0.288	1.60	1.78

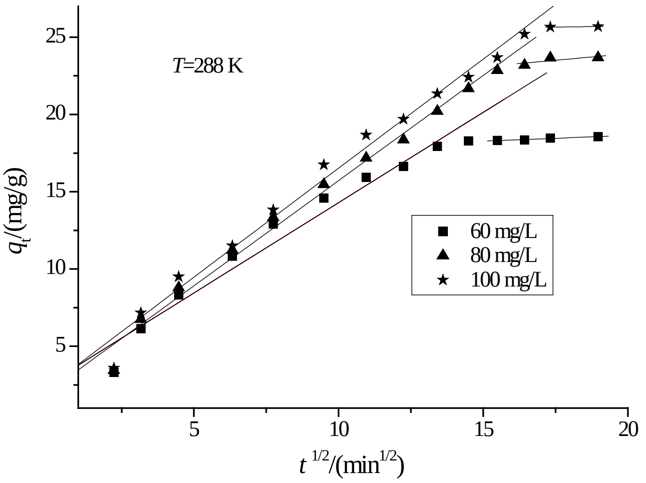


Fig. 6. Intraparticle diffusion plot for NR onto rice husk.

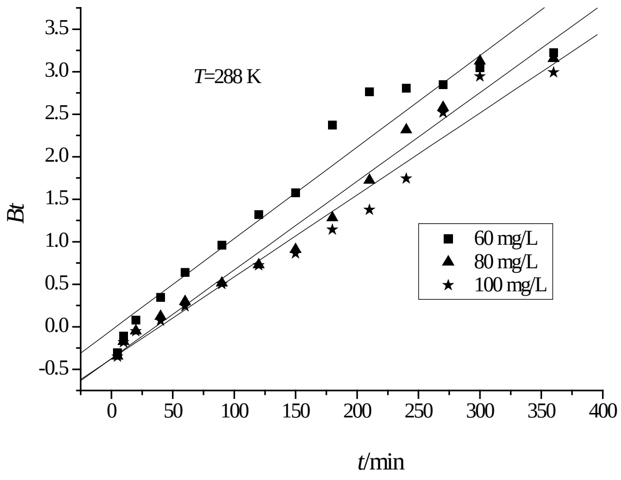


Fig. 7. Plot of Bt vs. t (Boyd plot).

Table 4
Parameters of intraparticle diffusion model

C_0	60 mg/L	80 mg/L	100 mg/L
$k_{i,1}$ (mg/g min$^{0.5}$)	1.17±0.08	1.36±0.05	1.41±0.05
C_1 (mg/g)	1.23±0.09	2.10±0.49	2.42±0.56
R	0.982	0.994	0.993
$k_{i,2}$ (mg/g min$^{0.5}$)	0.0732±0.011	0.087±0.04	0.088±0.04
C_2 (mg/g)	17.18±0.19	22.53±2.32	25.23±2.16
R	0.978	0.972	0.999

compute Bt, Eq. (7) is substituted into Eq. (8) and the kinetic expression becomes

$$Bt = -0.4997 - \ln\left(1 - \frac{q_t}{q_e}\right) \tag{9}$$

Thus, the value of Bt can be computed for each value of F, and then plotted against time to configure the Boyd plots. The linearity of these plots is employed to distinguish between external-transport-(film diffusion) and intraparticle-transport-controlled rates of adsorption. A straight line passing through the origin is shown that adsorption processes are governed by particle-diffusion mechanisms for the studied initial dye concentration; otherwise they are governed by film diffusion or external mass transport [29].

Fig. 7 shows the Boyd plots. The plots are linear in the initial period of adsorption and all their intercepts are not significantly different from zero, indicating that film diffusion is the rate limiting process. In the initial adsorption period, film-diffusion or chemical reaction may control the overall rate of adsorption. The presence of two pore diffusion periods in Fig. 6 indicates the presence of two pore diffusion parameters, $k_{i,1}$ and $k_{i,2}$ as shown in Table 4. The rate parameters $k_{i,1}$ and $k_{i,2}$ represented the diffusion of NR in pores that have two distinct sizes (macropores and mesopores) [30]. Therefore, the decrease in value of k for macropore to mesopore diffusion was a direct consequence of the relative free path for diffusion available in each pore size. Similar results were obtained by El-Kamash et al. [31] and Wang et al. [32].

Values of B were calculated from the slope of Bt vs. time plots (Fig. 7) and were0.00964, 0.01042, 0.01077 1/min at initial NR concentration of 60, 80, 100 mg/L, respectively.

The effective diffusion coefficient (D_i) was calculated according to values of B using the following relation [28]:

$$B = \frac{\pi^2 D_i}{r^2} \tag{10}$$

where D_i (cm^2/s^{-1}) is the effective diffusion coefficient of NR in the adsorbent and r is the average radius of adsorbent particle by sieve analysis (20—40 mesh, 30 mesh was chosen) and by assuming to be spherical. According to Singh et al. [33], a D_i value in the order of 10^{-11} cm^2/s is indicative of intraparticle diffusion as rate-limiting step. In this study, the values of D_i (1.46×10^{-8}, 1.58×10^{-8} and 1.64×10^{-8} cm^2/s, respectively, average 1.56×10^{-8} cm^2/s) obtained are in the order of 10^{-8} cm^2/s, which is larger than 3 orders of magnitude. This also indicates that the intraparticle diffusion is not the rate-controlling step. Similar results were found by Kumar et al. [34] and Hameed and El-Khaiary [35].

3.9. Comparison of adsorption capacity for NR with other adsorbents

The NR adsorption capacity of rice husk was compared to the adsorption capacities of some other adsorbents reported in literature. Differences of dye uptake are due to the properties of each adsorbent such as structure, functional groups and surface area.

Yuan [36] examined the adsorption of NR by ordered mesoporous carbons and found a 200 mg/g NR uptake capacity. Gong [37] used peanut husk as an adsorbent for the removal of dye and found 87.7 mg/g uptake capacity for NR. Compared to other adsorbents, the capacity of NR adsorption onto rice husk is relative lower. But as agricultural by-product, it is vast and cheap, so rice husk can be used to remove NR from the solution.

3.10. Thermodynamic parameters of adsorption

To estimate the effect of temperature on the adsorption of NR on rice husk, the free energy change (ΔG^0), enthalpy change (ΔH^0), and entropy change (ΔS^0) were determined. The adsorption process can be summarized which represents a heterogeneous equilibrium. The apparent equilibrium constant (K_c') of the adsorption is defined as [25,38–41]:

$$K_c' = c_{ad,e} / c_e \tag{11}$$

where $c_{ad,e}$ is the concentration of NR on the adsorbent at equilibriumn (mg/L). The value of K_c' in the lowest experimental NR concentration can be obtained [30]. The K_c' value is used in the following equation to determine the Gibbs free energy of biosorption (ΔG^0).

$$\Delta G^0 = -RT \ln K_c' \tag{12}$$

The enthalpy (ΔH^0) and entropy (ΔS^0) can be obtained from the slope and intercept of a van't Hoff equation of ΔG^0 vs. T:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{13}$$

where ΔG^0 is standard Gibbs free energy change, J; R is universal gas constant, 8.314 J/mol K and T is absolute temperature, K.

The thermodynamic parameters are listed in Table 5. The negative values of ΔG^0 at various temperatures are due to the fact that the adsorption processes are spontaneous and that the negative value of ΔG^0 decreased with an increase in temperature, indicating that the spontaneous nature of adsorption of NR is inversely proportional to the temperature.

Enhancement of adsorption capacity of the adsorbent at higher temperatures may be attributed to an enlargement of pore size and/or activation of the adsorbent surface. The positive values of ΔH^0 indicate the endothermic nature of the process whereas the positive ΔS^0 value confirms the increased randomness at the solid–solute interface during adsorption and reflects the affinity of the adsorbent material for dye. The low value of ΔS^0 also indicates that no remarkable change on entropy occurs.

Table 5
Thermodynamic parameters of NR adsorption on rice husk

T (K)	288	298	308
ΔG^0 (kJ/mol)	–8.92	–10.54	–12.51
ΔH^0 (kJ/mol)		42.77	
ΔS^0 (kJ/mol K)		0.179	

4. Conclusion

The present study showed that the rice husk can be used as an adsorbent for the removal of NR from its solution. The equilibrium data followed Langmuir isotherm confirming the monolayer coverage of NR onto rice husk. Kinetics data tend to fit well in pseudo-first-second-order and pseudo-second-order kinetic models. The process mechanism was found to be complex, consisting of both surface adsorption and pore diffusion. The process was spontaneous and endothermic in nature.

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