EQUILIBRIUM, KINETIC, AND THERMODYNAMIC STUDIES OF HAZARDOUS DYE NEUTRAL RED BIOSORPTION BY SPENT CORNCOB SUBSTRATE

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This study focuses on the possible use of spent corncob substrate (SCS), an agricultural waste utilized after the cultivation of white rot fungus *Pleurotus ostreatus*, to adsorb the hazardous dye Neutral Red (NR) from aqueous solutions. Natural SCS was initially characterized by using a combination of Fourier Transform Infrared Spectrometry (FTIR) and Brunauer-Emmett-Teller (BET) techniques. A batch adsorption study was carried out with varied solution pH, adsorption time, temperature, and initial NR concentration. It was found that NR uptake was favorable over a pH range of 4.0 to 7.0, and the equilibrium adsorption capacity can be reached within about 180 min. The biosorption data were also calculated by the pseudo-second-order kinetic model and Langmuir isotherm model. The maximum adsorption capacity was 139.1, 140.0, and 143.3 mg g^{-1} at 20, 30, and 40 °C, respectively. Thermodynamic parameters showed that the adsorption was a spontaneous and endothermic process. The study highlighted a new pathway to develop potential low-cost biosorbent for the removal of dye pollutants from wastewater.

Keywords: Biosorption; Neutral Red; Spent corncob substrate; Kinetics; Isotherms; Thermodynamics

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INTRODUCTION

Synthetic dyes are used in many industries such as food, paper, carpets, rubbers, plastics, cosmetics, and textiles in order to color their products. The colored water can affect plant life and thus can destroy an entire ecosystem. To avoid the environmental disaster engendered from the toxic chemical dyes, efficient and low-cost methods have to been developed to treat the industrial wastewater.

Neutral Red (NR, toluylene red chloride, $C_{15}H_{16}N_4{\cdot}HCl$, C.I.50040, Formula weight 288.78), a water-soluble cationic dye, is commonly used for counterstaining cell nuclei in biological research. It is a pH indicator with changing color from red to yellow over the pH range 6.8 to 8.0. Many natural polymers, such as pectin, cellulose, hemicelluloses, protein, chitosan, and chitin, are known to have binding groups for dye ions, e.g. carboxyl, hydroxyl and amidogen, etc., which makes it possible for the bio-resources containing such polymers to adsorb dye ions from wastewater. Besides their high adsorption capability and low costs, the biodegradable and nontoxic nature of the bio-resources is attracting people to exploit these materials to replace traditional adsorbents. From such a viewpoint, several studies have been devoted, during recent decades, to investigating the dye-binding efficiency of several biosorbents, such as sativa fruit (Thirumalisamy and Subbian 2010), hazelnut shells (Carletto et al. 2008), spent cottonseed hull substrate (Zhou et al. 2011) and jackfruit leaf powder (Uddin et al. 2009).

In continuation of these efforts, the spent mushroom substrate (SMS) after having been used for edible fungi cultivation was evaluated to determine its potential as a NR biosorbent. China is now the largest edible fungi producer, consumer, and exporter in the world. In 2008, China's mushroom production was over 17.3 million tons, accounting for about 70% of the total world output. In China, the total waste substrates after the edible fungi production have reached about 29 million tons every year, but most of them are abandoned. If the utilization of SMS can be realized, it will produce huge economic and ecological benefits.

In China, one of the popularly cultivated mushroom species is the white rot fungus *Pleurotus ostreatus* (*P. ostreatus*). It can be cultivated on a wide range of substrates such as corncobs, cottonseed hull, sawdust, or combinations of these ingredients. Among the various agricultural waste materials, corncob is a promising agricultural resource for mushroom cultivation due to the extensive cultivation of corn and because corncobs are rich in cellulose, hemicellulose, lignin, and protein contents (Li et al. 2001; Cha et al. 2010). It was also observed that the dry matter and cellulose, hemicellulose, lignin, and protein contents in corncob substrate changed considerably during the growing period of *P. ostreatus*. Thus utilizing spent corncob substrate (SCS) degraded after the cultivation of *P. ostreatus* as an alternative and low-cost biosorbent would increase economic value and help to reduce the cost of waste disposal. Besides this, the problem of environmental pollution would also be reduced considerably.

In this study, we explored the potential of using SCS as an adsorbent to remove NR dye from aqueous solutions. The equilibrium, kinetic, and thermodynamic data of the adsorption process were evaluated to study the adsorption mechanism of NR molecules onto the prepared SCS. Results of this study will be useful for future scale up using as a low-cost biosorbent for the removal of cationic dyes.

NOMENCLATURE

C_e	equilibrium liquid-phase solute concentration (mg L^{-1})
C_0	initial liquid-phase solute concentration (mg L^{-1})
p	adsorption ratio (%)
pH_f	value of final equilibrium pH
q_e	amount of adsorption at equilibrium (mg g^{-1})
q_t	amount of adsorption at time t (mg g^{-1})
k_1	pseudo-first-order rate constant (min^{-1})
k_2	pseudo-second-order rate constant (g mg^{-1} min^{-1})
k_p	intraparticle diffusion constant
q_{max}	maximum adsorption capacity of adsorbent per unit mass (mg g^{-1})
K_L	Langmuir constant
K_F	Freundlich constant
n	Freundlich isotherm constant related to adsorption intensity

$G°$ Gibbs free energy of adsorption (kJ mol^{-1})
$H°$ enthalpy of adsorption (kJ mol^{-1})
$S°$ entropy of adsorption (kJ mol^{-1} K^{-1})
R universal gas constant (8.314 J mol^{-1} K^{-1})
R^2 coefficient of determination

EXPERIMENTAL

Preparation of Biosorbent

The solid SCS of *P. ostreatus* was kindly provided by Pingdu Edible Fungi Ltd. (Shandong, China). The biomass was dried in an oven at 70 ℃ for 24 h, and then it was crushed in a knife-mill. The resulting material was sieved, and the portions with particle size lower than 250 μm were obtained. This produced a uniform material for the complete set of adsorption tests, which was then preserved in a glass bottle and used in the adsorption studies.

Chemicals

Neutral Red of analytically pure grade was used without further purification. The stock solution was prepared by dissolving accurately weighed NR in distilled water at the concentration of 1 g L^{-1}. The working solution was prepared by diluting the dye stock solution with distilled water to the required concentration. Fresh dilution was used for each adsorption study. The initial pH value of solution was adjusted with 0.10 mol L^{-1} NaOH or HCl solutions.

Biosorption Experiments

The batch equilibrium process was used to characterize the biosorption ability of SCS in a Shaking Water Bath (Julabo SW23, Germany) at 150 rpm for a period of time. In each adsorption experiment, SCS was added to 100 mL dye solution of determined initial concentration in a 250 mL conical flask. The influence of pH values, reaction time, and initial NR concentration on the adsorption capacity was investigated to optimize the biosorption conditions. After shaking the flasks for predetermined time intervals, the experimental biosorbent–dye mixtures were separated from the SCS by filtration with a stainless steel strainer (200 mesh), and then centrifuged at 7,500 rpm for 10 min in a centrifuge (Sigma 2-16KCH, Germany). The supernatants were analyzed to determine the residual NR concentration. The experiments were conducted in triplicate, and the negative controls (with no biosorbent) were simultaneously carried out to ensure that the biosorption was by SCS rather than the container. Following a systematic process, the biosorption uptake capacity of NR in batch system was tested.

Instrumental Analysis

FTIR spectra of SCS were obtained using a Fourier Transform Infrared Spectrometer (FTIR, Thermo Nicolet, Nexus) in the region of 400 to 4000 cm^{-1}. Approximately 1 mg of sample (≤2 μm) was mixed in 100 mg KBr to prepare the translucent sample disk. The spectra were recorded with a resolution of 4 cm^{-1}. Peak height and area were measured using the software ACD/SpecDB 11.0 Database File (Advanced Chemistry Development. Inc, USA).

The nitrogen sorption isotherms were measured by volumetric method on an automatic adsorption instrument (Micromeritics, Tristar 3000) at liquid nitrogen temperature (77 K). Specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method from the data in a P/P_0 range between 0.05 and 0.2. The sample was degassed at 180 ºC for 5 h prior to testing.

The remaining dye concentration in the supernatant was analyzed by using a UV-Vis spectrophotometer (Agilent 8453, USA) by monitoring the absorbance at a wavelength of maximum absorbance (530 nm). Calibration curves were obtained with standard NR solutions. In this work, the kinetics and equilibrium models were fitted by the software Microcal Origin 8.0.

RESULTS AND DISCUSSION

Characterization of SCS Adsorbent

The pH_{PZC} and BET surface area of SCS were found to be 4.20 and 1.0 m^2 g^{-1}, respectively. The FTIR spectra of the SCS adsorbents before and after adsorption of NR dye are shown in Fig. 1.

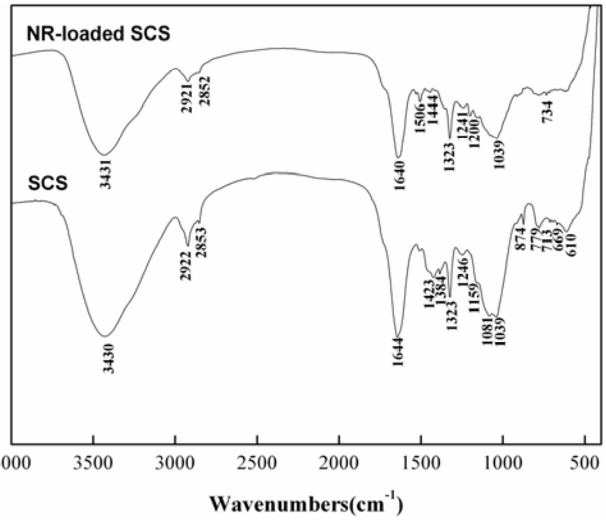

Fig. 1. FTIR spectra of SCS and NR-loaded SCS

For the pure SCS adsorbents, a broad absorption peak was observed at 3430 cm^{-1}, which corresponds to the vibration of –OH groups and –NH groups (Akar et al. 2009a). Two peaks at about 2922 and 2853 cm^{-1} are the characteristic stretching vibration of the methyl and methylene (CH_n) groups. The peak at 1644 cm^{-1} is characteristic of C=O bonds in aldehydes, ketones, or carboxylic acids. The absorption peaks around 1159 and 1081 cm^{-1} are assigned to the stretching vibration of P=O and P−OH bonds in phosphate group (Bayramoglu et al. 2006; Akar et al. 2009c). These functional groups on the SCS surface, such as –NH, －OH, C=O, COO^-, and －P=O, have been believed to be potential adsorption sites for entrapment of NR molecules. For the NR-loaded SCS, the peaks at 1640, 1506, 1444, 1241, and 1200 cm^{-1} had shifted or changed. These shifts or changes can be attributed to the changes in counter-ions associated with carboxylate, phosphate, and hydyroxylate anions, suggesting that acidic groups, both carboxyl and hydroxyl, are predominant contributors in NR ion uptake.

Batch Adsorption Studies

Influence of contact time and temperature

The influence of contact time on adsorption ratio of SCS was studied under the following experimental conditions: pH 7.0, initial NR concentration of 200 mg L^{-1}, and SCS dosage of 2.5 g L^{-1}. As shown in Fig. 2, the adsorption ratio of SCS increased instantly and reached a high value in the first 5 min adsorption stage. This means that a large number of vacant adsorption sites on the SCS surface were available at this stage. Thereafter, it became slower near the biosorption equilibrium (after 90 min), and the maximum adsorption ratio occurred within 180 min for all the temperature studied. After this period the amount of adsorbed NR did not significantly change with time due to the equilibrium of the repulsive forces between the NR ions on the solid and in the bulk phases. This trend indicated that the biosorbent was saturated with the adsorbate at this level. Based on the results, the adsorption time was fixed at 180 min for the rest of the batch experiments to make sure that adsorption equilibrium was reached.

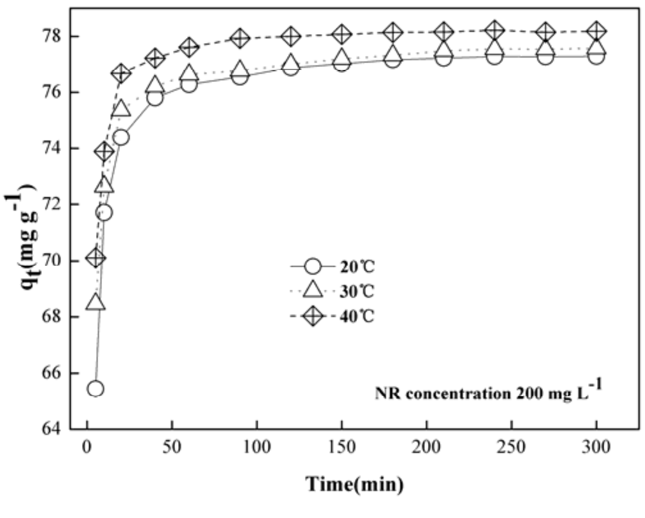

Fig. 2. Influence of reaction time on biosorption of NR on *SCS* (NR concentration 200 mg L^{-1}, *SCS* dosage 2.5 g L^{-1}, pH 7.0)

Additionally, an experiment was conducted to investigate the influence of temperature on the adsorption ratio. As presented in Fig. 2, the adsorption ratio of SCS at equilibrium increased slightly with the increase of the temperature over the range of 20 to 40 °C. Apparently, the equilibrium adsorption ratio of SCS was slightly influenced by the temperature change. This result is different from the reported studies (Akar et al. 2009b; Akar et al. 2009c), in which the adsorption ratio increases highly with the temperature rising. This may be ascribed to the fact that the amount or activity of SCS functional groups cannot be conspicuously increased correspondingly with the temperature increase from 20 to 40 °C. Furthermore, it was found that the adsorption rate increased obviously as the temperature increased from 20 to 40 °C in the first 60 min, indicating that the adsorption is an endothermic process (Akar et al. 2009b).

Influence of solution pH

Given that the pH value is an important parameter to influence the adsorption capacity of the biosorbents, herein, the NR adsorption ratio under different pH values was investigated. As NR is precipitated when pH is over 7, the effect of pH was analyzed over the range of pH 2 to 7 and shown in Fig. 3. As Fig. 3 indicates, the uptake of NR ions depends on pH, and at low pH value of 2.0, NR adsorbed a low amount of NR. When the initial pH of the NR solution increased, the adsorption capacity increased as well. A sharp increment in adsorption capacity was observed from pH 2.0 to 3.0, indicating that more NR was adsorbed on SCS at higher pH values. However, the uptake capacity did not change significantly from pH 4.0 to 7.0, and the amount of dye removed remained practically constant. The optimum pH for adsorption of NR by the SCS was pH 7 (96.7% adsorption). A similar phenomenon has been observed for the biosorption of NR from aqueous solutions by kohlrabi peel, peanut hull, spent cottonseed hull substrate (Akar et al. 2009b; Zhou et al. 2011; Gong et al. 2005, 2007). The pH_{PZC} of an adsorbent is a very important characteristic that determines the pH at which the adsorbent surface has net electrical neutrality. At this value, the acidic or basic functional groups no longer contribute to the pH of the solution. The pH of the solution affects the surface charge of the adsorbents as well as the degree of ionization of different pollutants (Ibrahim et al. 2010). The hydrogen and hydroxyl ions are adsorbed quite strongly, and therefore the adsorption of other ions is affected by the pH of the solution.

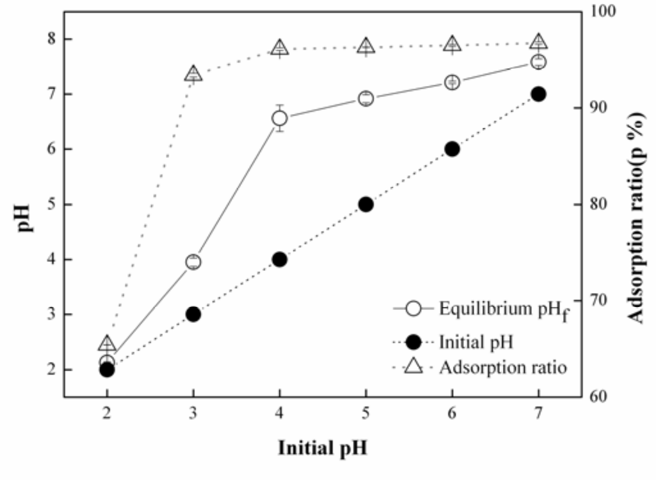

Fig. 3. Influence of solution pH on biosorption of NR by SCS (Reaction time 180 min, NR concentration 200 mg L^{-1}, SCS dosage 2.5 g L^{-1}, Temperature 30 ^{o}C)

Furthermore, the solution pH after adsorption (final equilibrium pH_f) was measured, and results are presented in Fig. 3. It can be observed that pH_f was higher than the initial pH. So this means that SCS has a significant capacity to buffer acidity, because SCS release OH^{-} ions into solution by alkaline groups such as hydroxyl and amino on the surface of the biosorbent when the solution pH was lower than the pH_{PZC} of SCS.

Influence of initial NR concentration

The results about the influence of the initial NR concentration on biosorption are shown in Fig. 4. First, the adsorption ratio remained constant for the initial concentrations from 20 to 200 mg L^{-1}. However, the NR adsorption ratio decreased gradually when the initial concentration increased from 300 to 500 mg L^{-1}. The equilibrium NR concentration (C_e) increased with increasing initial NR concentration (see Fig. 4). Under the same conditions, if the concentration of NR in solution was higher, the active sites of SCS were surrounded by many more NR ions, and the adsorption would proceed more sufficiently, but the equilibrium concentration would increase. So the values of C_e and q_e increased with increasing initial NR concentration.

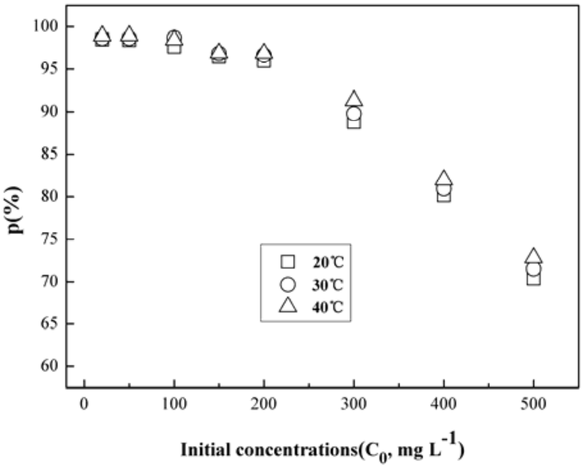

Fig. 4. Equilibrium adsorption quantity of NR at different initial concentration (Reaction time 180 min, *SCS* dosage 2.5 g L^{-1}, pH 7.0)

Kinetic Studies

The transient behavior of the batch biosorption process at different temperature was analyzed using the pseudo-first-order, the pseudo-second-order, and the intraparticle diffusion kinetic models.

The pseudo-first-order rate expression is given by the following equation (Girirajanna et al. 2010):

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{1}$$

The pseudo-second-order kinetic model is expressed as (Rao et al. 2010):

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

The intraparticle diffusion equation can be written as (Kumar et al. 2010):

$$q_t = k_p t^{\frac{1}{2}} + C \tag{3}$$

where q_t (mg g^{-1}) is the amount of solute adsorbed per gram of adsorbent over a time period t (min), and k_1 (min^{-1}) represents the first-order kinetic constant. k_2 (g mg^{-1} min^{-1}) is the second-order kinetic constant. k_p (g mg^{-1} min^{-1}) is the constant of intraparticle diffusion, and C is the intercept.

The constant k_2 is used to calculate the initial sorption rate h, at t→0, as follows (Vadivelan and Kumar 2005; El-Halwany 2010):

$$h = k_2 q_e^2 \tag{4}$$

Thus, the rate constant k_2, initial sorption rate h, and predicted q_e can be calculated from the plot of t/q versus time t using Eq. (2).

The kinetic constants of the fitting linear relationship of Eq. (1), Eq. (2), and Eq. (3) can be expected according to the results reported in Fig. 2, and are given in Fig. 5, Fig. 6, and Table 1.

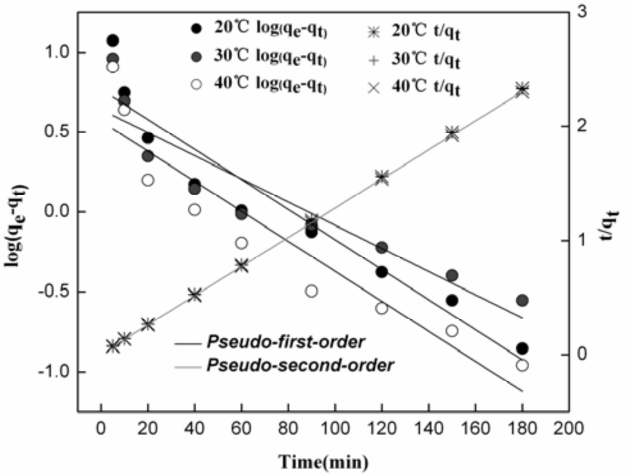

Fig. 5. Pseudo-first-order and pseudo-second-order kinetic functions of the adsorption of NR onto SCS

Table 1. Kinetic Parameters for Sorption of NR onto SCS versus Temperature

T (°C)	$q_{e,exp}$ (mg g^{-1})	Pseudo-first-order		Pseudo-second-order				The intraparticle diffusion	
		k_1 (min^{-1})	R_1^2	k$_2$ (g mg^{-1} min^{-1})	$q_{e,fitted}$ (mg g^{-1})	h (mg g^{-1} min^{-1})	R_2^2	k_p (mg g^{-1} min$^{-1/2}$)	R_p^2
20	77.3	0.02165	0.9099	0.0143	77.4	85. 7	1.0000	0.7608	0.5850
30	77.6	0.01667	0.8412	0.0185	77.5	111.1	0.9999	0.5875	0.5993
40	78.2	0.02160	0.8694	0.0227	78.4	139.5	1.0000	0.5337	0.5760

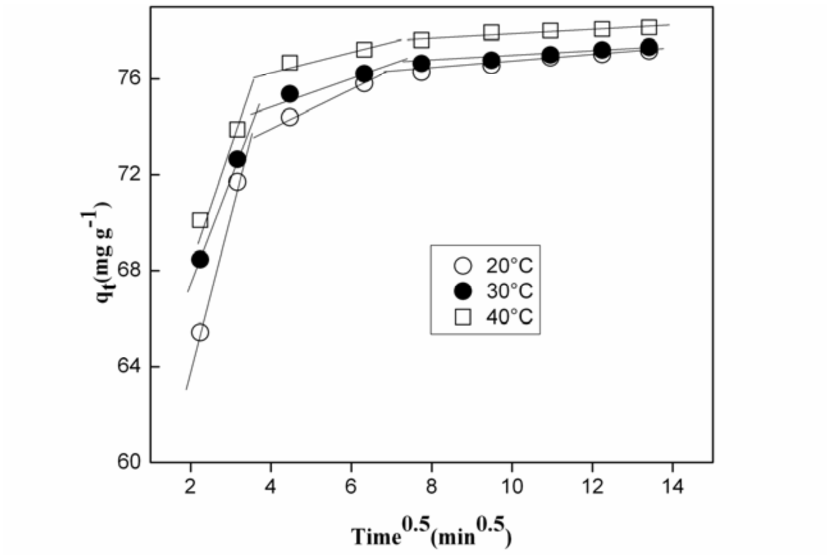

Fig. 6. Intraparticle diffusion plots for the adsorption of NR onto SCS

From Fig. 5, Fig. 6, and Table 1, it is observed that R_2^2, in the range of 0.9999 to 1, was higher than R_1^2 and R_p^2 at various temperature, and the fitted $q_{e,fitted}$ values from the pseudo-second-order kinetic model were very close to the experimental $q_{e,exp}$ values. The higher values of R_2^2 mean that the adsorption process follows a pseudo-second-order mechanism. Also this suggests an assumption that underlies the pseudo-second-order model, i.e. that the NR uptake is controlled by a chemical process (Wan et al. 2010). Chemical adsorption can occur by the polar functional groups of lignin, which includes alcohols, aldehydes, ketones, acids, phenolic hydroxides, and ethers as chemical bonding agents (Vadivelan and Kumar 2005). From Table 1, it is also observed that the initial sorption rate h, and pseudo-second-order-rate constant k_2 increased with the solution temperature from 20 to 40 °C. These findings indicate that increasing temperature may increase the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particles, owing to the decrease in the viscosity of the solution.

The intraparticle diffusion model is based on the transfer of matter from the external surface to the surface inside the pores (Li et al. 2009). According to the experiments, it is noted that the adsorption process tended to proceed in three consecutive phases. The first step is attributed to the external surface adsorption or the instantaneous adsorption. The second step is the gradual adsorption stage, where intra-particle diffusion is rate-limiting. The third step is the final equilibrium stage, where intra-particle diffusion starts to slow down due to the extremely low adsorbate concentration left in the solution. One or more of the three steps control the whole adsorption rate. A similar conclusion was reached in earlier studies of the adsorption of Neutral Red from aqueous solution onto peanut husk (Han et al. 2008) and halloysite nanotubes (Luo et al. 2010).

Equilibrium Studies

Determination of adsorption isotherm model constants about NR/SCS system

The analysis of biosorption process requires a better understanding of the adsorption process. Equilibrium isotherm equations are used to describe the experimental sorption data (Han et al. 2007).

A dynamic equilibrium is established in the concentration of adsorbate between two phases. The equilibrium isotherm is of fundamental importance for the design and optimization of the adsorption system for the removal of NR from aqueous solution. Therefore, it is necessary to establish the most appropriate correlation for the equilibrium curves. In the present study, the biosorption equilibrium was described by use of Langmuir and Freundlich equilibrium models (Thirumalisamy and Subbian 2010).

The Langmuir adsorption isotherm has been successfully applied to many pollutants adsorption processes and is the most widely used adsorption isotherm for the adsorption of a solute from a liquid solution. A basic assumption of the Langmuir theory is that adsorption takes place at specific homogeneous sites within the adsorbent. The saturated monolayer isotherm can be represented as,

$$q_e = \frac{q_{max} K_L C_e}{1 + KC_e} \tag{5}$$

where q_{max} and K_L are the Langmuir model constants. These constants are called the adsorption capacity (maximum surface coverage) and bonding energy constant, respectively. The Langmuir adsorption isotherm has traditionally been used to quantify and contrast the performance of different adsorbents. It has served to estimate the maximum dye uptake values where they could not be reached in the experiments (Vijayaraghavan et al. 2008).

The Freundlich isotherm is an empirical expression that encompasses the heterogeneity of the surface and an exponential distribution of the sites and their energies. This isotherm has been further extended by considering the influence of adsorption sites and the competition between different adsorbents for adsorption on the available sites. Freundlich isotherm has been observed to be applicable for a wide range of heterogeneous surfaces including activated carbon, silica, clays, and polymers. The Freundlich equation can be written as,

$$q_e = K_F C_e^{\frac{1}{n}} \tag{6}$$

where $1/n$ is the heterogeneity factor of the adsorbent and K_F is a constant. The surface heterogeneity is due to the existence of crystal edges, types of cations, surface charges, surface modification groups, and degrees of crystallinity of the surface. The $1/n$ value indicates the relative distribution of energy sites and depends on the nature and strength of the adsorption process.

Herein, model constants were calculated according to Eqs. (5) and (6) by the non-linear regression analysis of the batch biosorption data in Fig. 4. The comparisons between experimental data and theoretical plots of Langmuir and Freundlich isotherm models, the model constants, along with their coefficients of determination (R^2) for biosorption of NR onto SCS, are presented in Fig. 7 and Table 2.

The coefficient of determination for the Langmuir model, R_L^2, varied from 0.9832 to 0.9909, while for Freundlich it varied from 0.9434 to 0.9452. The comparison of correlation coefficients (R^2) of the nonlinearized form of both equations in Table 2 suggests that the Langmuir isotherm may be a suitable model, and also that the adsorption of NR on SCS takes place as monolayer adsorption on a surface that is homogenous in adsorption affinity (Hameed 2009b; Hameed 2009a). The maximum monolayer adsorption capacities were found between 139.1 and 143.3 mg g^{-1} at the temperatures 20, 30, and 40 °C used in this study. The increasing q_{max} values of adsorption with the increasing temperature indicated that the process is endothermic in nature.

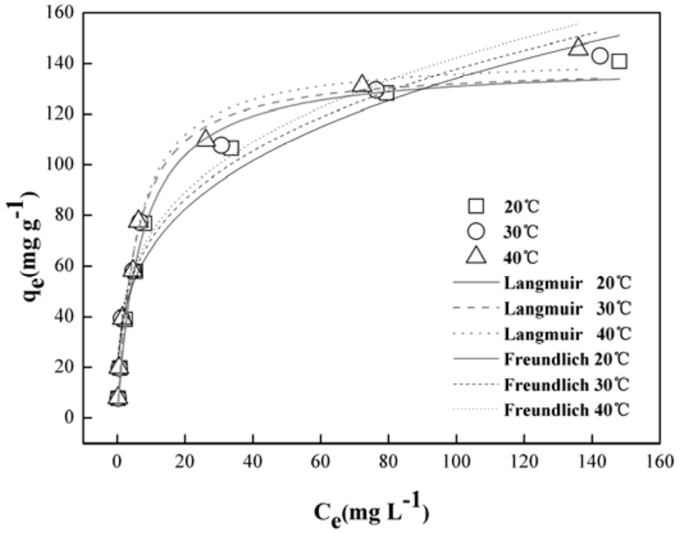

Fig. 7. Langmuir and Freundlich adsorption isotherms of NR on SCS

Table 2. Isotherm Model Constants for the Batch and Continuous Mode Biosorption of NR onto SCS

T (°C)	Langmuir constants			Freundlich constants		
	q_{max} (mg g^{-1})	K_L (L mg^{-1})	R_L^2	n	K_F	R_F^2
20	139.1	0.1429	0.9909	3.30	33.2	0.9452
30	140.0	0.1769	0.9832	3.44	36.1	0.9434
40	143.3	0.1827	0.9901	3.44	37.3	0.9450

THERMODYNAMICS STUDIES

The amount of NR adsorbed onto SCS at equilibrium at different temperature was examined to obtain thermodynamic parameters. Changes in the free energy (Δ*G*°), enthalpy (Δ*H*°) and entropy (Δ*S*°) were evaluated using the following equations and calculated from a plot of Δ*G*° against *T* (Luo et al. 2010; Akar et al. 2009c):

$$\Delta G^\circ = -RT \ln K_L \qquad (7)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \qquad (8)$$

where K_L is the Langmuir constant when concentration terms are expressed in L mol^{-1}, R (8.314 J/mol K) is the universal gas constant, and T is the temperature (K).

Table 3. Thermodynamic Parameters Calculated from Langmuir Constant (K_L) for NR Adsorption onto SCS

Temperature (K)	Δ*G*° (kJ/mol)	Δ*H*° (kJ/mol)	Δ*S*° (kJ/mol K)
293	-25.9	9.19	0.12
303	-27.3		
313	-28.3		

As can be seen from Table 3, the positive value of Δ*H*° confirms the endothermic character of NR biosorption, whereas the negative value of Δ*G*° indicates the spontaneity and feasibility of the biosorption process. The trend toward more negative values of Δ*G*° with increasing temperature reveals that adsorption of NR onto SCS becomes more favorable at higher temperature. A low value of ΔS° indicates that there is no remarkable change on entropy associated with the biosorption, and the positive Δ*S*° values reflect affinity of the adsorbent for NR.

CONCLUSIONS

1. The adsorption capacity of NR adsorbed onto the SCS adsorbent was observed to be related to the solution pH, reaction time, and NR initial concentration.
2. The functional groups on the biosorbent surface were found to play a role in the entrapment of the target NR molecules. Since SCS used in this work is freely, abundantly, and locally available, the resulting biosorbent is expected to be economically viable for removal of NR dye from aqueous solution.
3. The kinetic study of NR adsorption onto the SCS adsorbent revealed that the pseudo-second order model yields a much better fit than the pseudo-first order model. Intraparticle diffusion analysis demonstrates that NR diffuses quickly among the particles at the beginning of the adsorption process, and then the diffusion slows down and stabilizes.
4. Results obtained were modeled using Langmuir and Freundlich isotherms. The equilibrium data were well fitted with a Langmuir isotherm equation according to the nonlinear curve fitting regressive analysis, indicating that monolayer maximum adsorption capacity of NR onto SCS is as high as 143.3 mg g^{-1}.
5. The positive value of Δ*H*° confirmed the endothermic nature of the adsorption interaction whereas the positive Δ*S*° value showed the increased randomness at the solid–solution interface during the adsorption process. The negative value of Δ*G*° indicated the feasibility and the spontaneous nature of the adsorption of NR onto SCS.

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REFERENCES CITED

Akar, S., Gorgulu, A., Kaynak, Z., Anilan, B., and Akar, T. (2009a). "Biosorption of Reactive Blue 49 dye under batch and continuous mode using a mixed biosorbent of macro-fungus *Agaricus bisporus* and *Thuja orientalis* cones," *Chem. Eng. J.* 148**,** 26-34.

Akar, T., Anilan, B., Gorgulu, A., and Akar, S. T. (2009b). "Assessment of cationic dye biosorption characteristics of untreated and non-conventional biomass: Pyracantha coccinea berries," *J. Hazard. Mater.* 168**,** 1302-1309.

Akar, T., Tosun, I., Kaynak, Z., Kavas, E., Incirkus, G., and Akar, S. T. (2009c). "Assessment of the biosorption characteristics of a macro-fungus for the decolorization of Acid Red 44 (AR44) dye," *J. Hazard Mater* 171**,** 865-71.

Bayramoglu, G., Celik, G., and Arica, M. Y. (2006). "Biosorption of Reactive Blue 4 dye by native and treated fungus *Phanerocheate chrysosporium*: Batch and continuous flow system studies," *J. Hazard. Mater.* 137**,** 1689-1697.

Carletto, R. A., Chimirri, F., Bosco, F., and Ferrero, F. (2008). "Adsorption of congo red dye on hazelnut shells and degradation with *Phanerochaete chrysosporium*," *BioResources* 3**,** 1146-1155.

Cha, W. S., Park, S. S., Kim, S. J., and Choi, D. (2010). "Biochemical and enzymatic properties of a fibrinolytic enzyme from *Pleurotus eryngii* cultivated under solid-state conditions using corn cob," *Bioresour. Technol.* 101**,** 6475-6481.

El-Halwany, M. M. (2010). "Study of adsorption isotherms and kinetic models for Methylene Blue adsorption on activated carbon developed from Egyptian rice hull (Part II)," *Desalination* 250**,** 208-213.

Girirajanna, A., Prasad, D., and Abdullah, M. A. (2010). "Biosorption of Cr(VI) from synthetic wastewater using the fruit shell of gulmohar (*Delonix regia*): Application to electroplating wastewater," *BioResources* 5**,** 838-853.

Gong, R. M., Li, M., Yang, C., Sun, Y. Z., and Chen, J. (2005). "Removal of cationic dyes from aqueous solution by adsorption on peanut hull," *J. Hazard. Mater.* 121**,** 247-250.

Gong, R. M., Zhang, X. P., Liu, H. J., Sun, Y. Z., and Liu, B. R. (2007). "Uptake of cationic dyes from aqueous solution by biosorption onto granular kohlrabi peel," *Bioresour. Technol.* 98**,** 1319-1323.

Hameed, B. H. (2009a). "Evaluation of papaya seeds as a novel non-conventional low-cost adsorbent for removal of methylene blue," *J. Hazard. Mater.* 162**,** 939-944.

Hameed, B. H. (2009b). "Grass waste: A novel sorbent for the removal of basic dye from aqueous solution," *J. Hazard. Mater.* 166**,** 233-238.

Han, R., Han, P., Cai, Z., Zhao, Z., and Tang, M. (2008). "Kinetics and isotherms of Neutral Red adsorption on peanut husk," *J Environ Sci (China)* 20**,** 1035-1041.

Han, R. P., Zou, W. H., Yu, W. H., Cheng, S. J., Wang, Y. F., and Shi, J. (2007). "Biosorption of methylene blue from aqueous solution by fallen phoenix tree's leaves," *J. Hazard. Mater.* 141**,** 156-162.

Ibrahim, M. N. M., Ngah, W. S. W., Norliyana, M. S., Daud, W. R. W., Rafatullah, M., Sulaiman, O., and Hashim, R. (2010). "A novel agricultural waste adsorbent for the removal of lead (II) ions from aqueous solutions," *J. Hazard. Mater.* 182**,** 377-385.

Kumar, P. S., Ramalingam, S., Senthamarai, C., Niranjanaa, M., Vijayalakshmi, P., and Sivanesan, S. (2010). "Adsorption of dye from aqueous solution by cashew nut shell: Studies on equilibrium isotherm, kinetics and thermodynamics of interactions," *Desalination* 261**,** 52-60.

Li, X., Pang, Y., and Zhang, R. (2001). "Compositional changes of cottonseed hull substrate during P. ostreatus growth and the effects on the feeding value of the spent substrate," *Bioresour. Technol.* 80**,** 157-161.

Li, Z., Tang, X., Chen, Y., Wei, L., and Wang, Y. (2009). "Activation of *Firmiana Simplex* leaf and the enhanced Pb(II) adsorption performance: Equilibrium and kinetic studies," *J. Hazard. Mater.* 169**,** 386-94.

Luo, P., Zhao, Y., Zhang, B., Liu, J., and Yang, Y. (2010). "Study on the adsorption of Neutral Red from aqueous solution onto halloysite nanotubes," *Water Res.* 44**,** 1489-1497.

Rao, K. S., Anand, S., and Venkateswarlu, P. (2010). "Adsorption of cadmium(II) ions from aqueous solution by *Tectona grandis* LF (teak leaves powder)," *BioResources* 5**,** 438-454.

Thirumalisamy, S., and Subbian, M. (2010). "Removal of methylene blue from aqueous solution by activated carbon prepared from the peel of cucumis sativa fruit by adsorption," *BioResources* 5**,** 419-437.

Uddin, M. T., Rukanuzzaman, M., Khan, M. M. R., and Islam, M. A. (2009). "Adsorption of methylene blue from aqueous solution by jackfruit (*Artocarpus heteropyllus*) leaf powder: A fixed-bed column study," *J. Environ. Manage.* 90**,** 3443-3450.

Vadivelan, V., and Kumar, K. V. (2005). "Equilibrium, kinetics, mechanism, and process design for the sorption of methylene blue onto rice husk," *J. Colloid Interface Sci.* 286**,** 90-100.

Vijayaraghavan, K., Won, S. W., Mao, J., and Yun, Y. S. (2008). "Chemical modification of *Corynebacterium glutamicum* to improve methylene blue biosorption," *Chem. Eng. J.* 145**,** 1-6.

Wan, M. W., Kan, C. C., Rogel, B. D., and Dalida, M. L. P. (2010). "Adsorption of copper (II) and lead (II) ions from aqueous solution on chitosan-coated sand," *Carbohydr. Polym.* 80**,** 891-899.

Zhou, Q., Gong, W., Xie, C., Yang, D., Ling, X., Yuan, X., Chen, S., and Liu, X. (2011). "emoval of Neutral Red from aqueous solution by adsorption on spent cottonseed hull substrate," *J. Hazard. Mater.* 185**,** 502-506.

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