Short communication

Removal of Neutral Red from aqueous solution by adsorption on spent cottonseed hull substrate

Zhou Qi [a], Gong Wenqi [a,*], Xie Chuanxin [b], Yang Dongjiang [c], Ling Xiaoqing [a], Yuan Xiao [a], Chen Shaohua [a], Liu Xiaofang [d]

[a] School of Resources and Environmental Engineering, Wuhan University of Technology, Luoshi Road 122, Wuhan, Hubei 430070, PR China
[b] SINOPEC Research Institute of Safety Engineering, Qingdao 266071, PR China
[c] Environmental Futures Centre and Griffith School of Environment, Gold Coast Campus, Griffith University, QLD 4222, Australia
[d] School of Chemical Engineering, Wuhan University of Technology, Wuhan 430070, PR China

ARTICLE INFO

ABSTRACT

Cottonseed hull, a low-cost widely available agricultural waste in China, after used as substrate for the white rot fungus Pleurotus ostreatus cultivation, was tested for the removal of Neutral Red (NR), a cationic dye, from aqueous solution. A batch adsorption study was carried out with varied solution pH, adsorbent dosage, reaction time and initial NR concentration. The results show that the kinetics of dye removal by the spent cottonseed hull substrate (SCHS) is prompt in the first 5 min and the adsorption equilibrium can be attained after 240 min. The biosorption kinetics and equilibrium follow typical pseudo-second-order and Langmuir adsorption models. Thermodynamic parameters of $\Delta G°$, $\Delta H°$ and $\Delta S°$ show that the adsorption is a spontaneous and endothermic process. Fourier transform infrared (FTIR) spectroscopy was used for the characterization of possible dye–biosorbent interaction. This study provides a facile method to produce low-cost biosorbent for the purification of dye contaminated water.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

In textile industry, the modern dyeing processes and machinery are designed for using synthetic dyes. Dye-containing wastewater discharged from such industry is a serious threat to the receiving water bodies around the industrial areas [1], because these toxic organic dyes can affect plant life and thus destroy the entire ecosystem [2]. To avoid the environmental disaster engendered from the toxic chemical dyes, efficient and low-cost methods have to be developed to clean 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 nuclear in biological research. It is a pH indicator with changing color from red to yellow over the pH range 6.8–8.0. NR has the structure as follows:
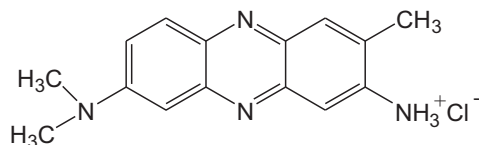
Many natural polymers, such as pectin, cellulose, hemicelluloses, protein, chitosan and chitin, are known to have binding groups for dye ions, e.g. carboxyl, hydroxyl and amidogen, etc., which make it possible for the bio-resources containing such polymers to adsorb dye ions from wastewater. Besides their high adsorption capability and low costs, the biodegradable and non-toxic nature of the bio-resources are attracting people to exploit these materials to replace the traditional adsorbents. From such a viewpoint, several studies have been devoted during recent years to investigating dye-binding efficiency of several biosorbents, such as peanut hull [3], peanut husk [4] and kohlrabi peel [5]. In continuation of these efforts, the spent mushroom substrate (SMS) after being used for edible fungi cultivation was also evaluated to determine its potential as a NR biosorbent.

The edible fungi are delicious vegetable grown in almost all regions of the world. 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 amount of the waste substrates after the edible fungi production has reached about 29 million tons every year, but most of them were abandoned. If the SMS can be reused, it will produce huge economic and ecological benefits.

In China, one of the popularly cultivated mushroom species is Pleurotus ostreatus, which belongs to the genus of the white rot fungus. It can be cultivated on a wide range of substrates such as corn

cobs, cottonseed hull, sawdust or combinations of these ingredients. Previous research has shown that cottonseed hull possesses advantages as a substrate material due to its high waterholding capability and nitrogen content [6]. In China, *P. ostreatus* is often cultivated on cottonseed hull as substrate. It has been observed that the dry matter and cellulose, hemicellulose, lignin, and protein contents in cottonseed hull substrate change considerably during *P. ostreatus* growing period. The total dry matter of cottonseed hull substrate decreases after the cultivation is completed. The spent substrate needs to be treated properly in order to minimize its possible adverse effects on the environment.

In this study, an attempt was made to use the spent cottonseed hull substrate (SCHS) after used for *P. ostreatus* cultivation as adsorbent in its natural form to remove NR. Batch adsorption experiments were carried out to study the feasibility.

2. Materials and methods

2.1. Biosorbent material and dye solutions

The solid SCHS for *P. ostreatus* cultivation was kindly provided by the Pingdu Edible Fungi Ltd. (Shandong, China). The biomass was dried in an oven at 70 °C for a period of 24 h, and then crushed in a knife-mill. The resulting material was sieved, and the portions with particle size lower than 250 μm were kept. This produced a uniform material for the complete set of adsorption tests, which was preserved in a glass bottle and used in the subsequent adsorption studies. Different from the conventional porous adsorbent, the specific surface area of SCHS adsorbent is lower than 1 m^2/g.

Neutral Red of analytically pure grade was used without further purification. The stock solution was prepared by dissolving accurately weighted NR in distilled water to the concentration of 1 g/L. 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 NaOH or HCl solutions.

2.2. Adsorption experiments

The batch equilibrium process was used to characterize the biosorption ability of SCHS in a shaking water bath (Julabo SW23, Germany) at 150 rpm for a period of time. In each adsorption experiment, SCHS was added to 100 mL dye solution of known initial concentration in a 250 mL conical flask and the effects of pH values, SCHS dosage, reaction time, and initial NR concentration were investigated to optimize the biosorption conditions. After shaking the flasks for predetermined time intervals, the experimental biosorbent–dye mixtures were separated from the SCHS by filtration with stainless steel strainer, and then centrifuged at 7500 rpm for 10 min in a centrifuge (Sigma 2-16KCH, Germany). The supernatants were analyzed using a UV–vis spectrophotometer (Agilent 8453, USA) at λ_{max} 530 nm to determine the residual NR concentration (C_e, mg/L). In this work, the kinetics, equilibrium and thermodynamic models were fitted by the software Microcal Origin 8.0.

The parameters selected for the materials and experiments, such as shaking water bath speed at 150 rpm and material particle size lower than 250 μm, were determined according to the literature and preliminary experiments [3,5].

2.3. Fourier transform infrared (FTIR) spectroscopic analysis and BET test

FTIR spectroscopy (Thermo Nicolet, Nexus, USA) was done to identify the functional groups present on native SCHS. IR absorbance data were obtained for wavenumbers in the range
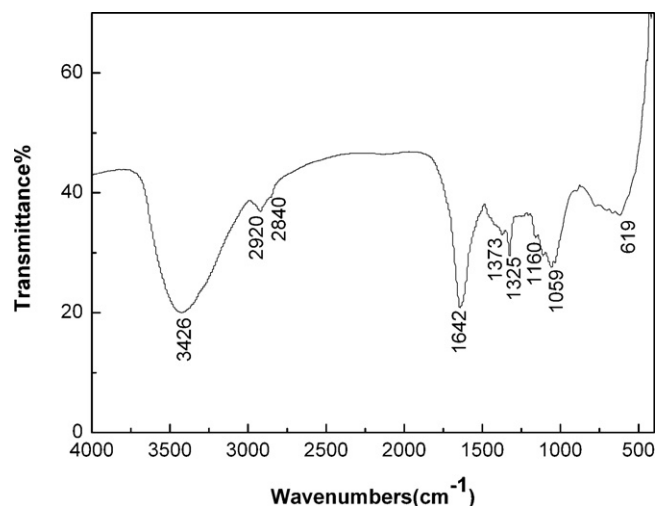

Fig. 1. FTIR spectrum of SCHS.

of 400–4000 cm^{-1} and analyzed using software ACD/SpecDB 11.0 Database File (Advanced Chemistry Development, Inc, USA). Approximately 1 mg of sample ($\leq$2 μm) was mixed in 100 mg KBr in order to prepare the translucent sample disk.

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 °C for 5 h prior to test.

3. Results and discussion

3.1. FTIR spectroscopy of SCHS

As shown in FTIR spectrum (Fig. 1), the existence of the functional groups on the SCHS surface and their responsibility for NR biosorption are supported. It has previously been reported that all of the biosorbent materials have intense absorption bands around 3500–3200 cm^{-1}, which represent the stretching vibrations of amino groups. These bands are superimposed onto the side of the hydroxyl group band at 3500–3300 cm^{-1} [7,8]. A similar and very broad absorption peak is observed for SCHS at 3426 cm^{-1} and this is indicative of the presence of –OH groups and –NH groups [9,10]. Two peaks at about 2920 and 2840 cm^{-1} show the characteristic stretching vibrations of the methyl and methylene (CH$_n$) groups. The peak at 1642 cm^{-1} is the characteristics of C=O bonds in acylamide function. These FTIR results indicate that there are

functional groups such as –NH, –OH, C=O and $R{-}\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}{-}NH_2$ in the biosorbent SCHS, which are potential adsorption sites for interaction with NR dye.

3.2. Influence of solution pH

The experiments were only conducted from pH 2.0 to 7.0 to avoid NR precipitation. Fig. 2 shows the effect of pH on NR adsorption onto SCHS and the shifts in pH after adsorption (pH$_f$). It can be observed that the solution pH affects the removal efficiency (p%) significantly with the increase of pH value from 2.0 up to 4.0. However, the uptake capacity does not change significantly from 4.0 to 7.0 and the amount of dye removal is kept practically constant (variations lower than 0.5%). Several reasons may be attributed to the NR adsorption behavior on the biosorbent rel-
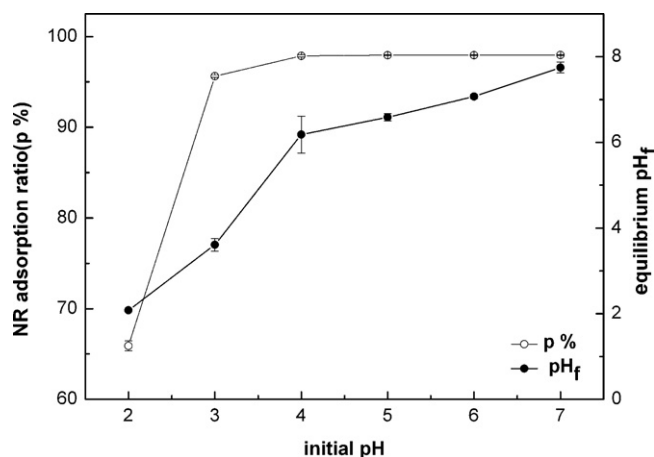
Fig. 2. Influence of solution pH on biosorption of NR by SCHS (reaction time 240 min, NR concentration 200 mg/L, SCHS dosage 2.5 g/L, and temperature 30 °C).
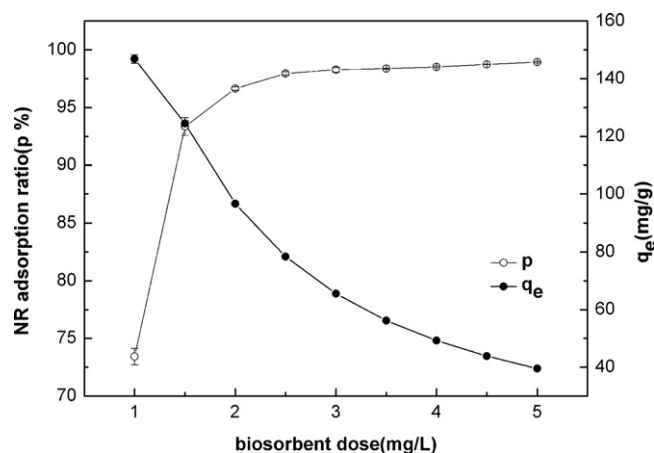

Fig. 3. Influence of SCHS dosage on biosorption amount and ratio of NR (reaction time 240 min, NR concentration 200 mg/L, pH 7.0, and temperature 30 °C).
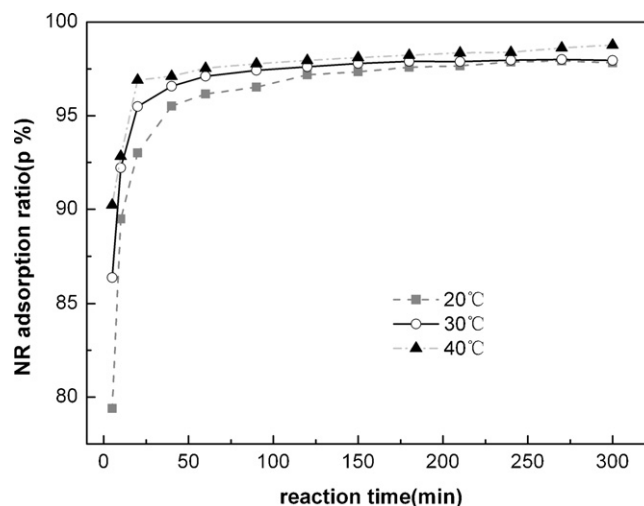
ative to solution pH. NR is a cationic dye, which exists in aqueous solution in the form of positively charged ions. The surface of SCHS may contain a large number of active sites, such as carboxyl and hydroxyl groups and the solute (NR ions) uptake can be related to the active sites. At lower pH, the surface of the biosorbent would also be surrounded by the excess hydronium ions, which competes with NR cations for active biosorption sites. At higher pH the surface of SCHS particles may become negatively charged, which enhanced the adsorption of the dye cations through electrostatic attraction.

It can be observed that the final equilibrium pH_f was higher than the initial pH. So this means that SCHS has a significant capacity to buffer acidity because there is a possibility that SCHS release OH⁻ ions into solution by alkaline groups such as hydroxyl and amino on the surface of the biosorbent. Similar results were also observed on the spent mushroom compost [11] and macrofungus biomass [12].

3.3. Influence of SCHS dosage

Fig. 3 shows the effect of adsorbent dosage on the removal of NR. It can be seen that the percentage removal of NR increases with the increase of the biosorbent dosage. The percent removal efficiency of NR increases from 73% to 99% when the biosorbent dosage increases from 1.0 to 5.0 g/L. On the other hand, the plot of biosorption amount vs. the biosorbent dosage shows that with increasing SCHS dosage from 1.0 to 5.0 g/L, the amount of adsorbed NR per gram SCHS at equilibrium (q_e, mg/g) decreases from 147 to 40 mg/g. When the dosage of the biosorbent is more than 2.5 g/L, the NR adsorption ratio vs. biosorbent dose curve reaches a plateau. So, the biosorbent amount of 2.5 g/L was chosen for the following experiments. The primary factor accounting for this characteristic was that adsorption sites remained unsaturated during the adsorption reaction, whereas the number of sites available for adsorption increased by increasing the SCHS dosage.

Fig. 4. Influence of reaction time on biosorption of NR on SCHS (NR concentration 200 mg/L, SCHS dosage 2.5 g/L, and pH 7.0).

3.4. Influence of contact time and biosorption kinetics

Fig. 4 shows that the biosorption capacity of SCHS increases instantly and reaches a high value at the initial stage (within 5 min) of the contact period at all studied temperatures. This indicates a large number of vacant sites on the SCHS surface are available during the initial biosorption stage. Thereafter, the biosorption becomes slower near the equilibrium and the maximum removal of NR occurs within 240 min. After this period, the amount of adsorbed NR does not significantly change due to the equilibrium of the repulsive forces between the NR ions on the surface and in the solution. This trend indicates that the biosorbent is saturated with the adsorbate at this level. The kinetics data in Fig. 4 were also analyzed using the pseudo-first order and the pseudo-second order models [13]. The results are shown in Table 1. The higher values

Table 1
Kinetics parameters for the adsorption of NR onto SCHS.

T (°C)	$q_{e,exp}$ (mg/g)	Pseudo-first order $\log(q_e - q_t) = \log q_e - k_1 t/2.303$			Pseudo-second order $t/q_t = 1/(k_2 q_e^2) + t/q_e$		
		$q_{e,fitted}$ (mg/g)	k_1 (min⁻¹)	R_1^2	$q_{e,fitted}$ (mg/g)	k_2 (g mg⁻¹ min⁻¹)	R_2^2
20	78.3	6.82	0.0183	0.927	78.6	0.0104	0.9999
30	78.4	3.56	0.0152	0.851	78.6	0.0190	1
40	79.0	3.04	0.0100	0.758	78.7	0.0221	1

Table 2
Biosorption isotherm constants for the biosorption of NR onto SCHS.

T (°C)	$q_{e,exp}$ (mg/g)	Langmuir equation $q_e = q_{max}K_L C_e/(1 + K_L C_e)$			Freundlich equation $q_e = K_F C_e^{1/n}$		
		q_{max} (mg/g)	K_L (L/mg)	R_L^2	K_F (mg/g (mg/L)$^{-1/n}$)	$1/n$	R_F^2
20	157.0	166.7	0.182	0.9688	46.7	0.280	0.8042
30	163.3	174.7	0.186	0.9822	47.9	0.294	0.8289
40	166.0	176.9	0.205	0.9666	49.6	0.293	0.8124

of R_2^2 were close to unity. Additionally, the fitted $q_{e,fitted}$ values were very close to the experimental $q_{e,exp}$ values. Apparently, the adsorption process follows a typical pseudo-second order kinetic model.

3.5. Influence of initial concentration and temperature

The influence of initial NR concentration on adsorption percentage of dyes was investigated. As shown in Fig. 5, the NR adsorption ratio is constant for initial concentrations from 50 to 250 mg/L, while the NR adsorption ratio decreases when the initial concentration increases from 250 to 500 mg/L. Temperature also has important effect on the biosorption process. The adsorption capacity (q_e) is found to increase with the temperature increase. Based on the data in Fig. 5, Langmuir equation and Freundlich equation [14] were employed to study the adsorption isotherm of dyes using non-linear regression analysis. The comparison between experimental data and theoretical plots of Langmuir and Freundlich isotherm models, the model constants, along with their correlation coefficients (R^2) for biosorption of NR onto SCHS, are presented in Fig. 6 and Table 2. The comparison of correlation coefficients (R^2) of the nonlinearized form of both equations indicates that the Langmuir model yielded a better fit for the experimental equilibrium adsorption data than the Freundlich model. The maximum biosorption capacity was found to be 166.7 mg/g, 174.7 mg/g and 176.9 mg/g at the temperatures of 20, 30 and 40 °C, respectively. Varying values of the Langmuir sorption capacity q_{max} for different biosorbents have been reported in the literature, such as kohlrabi peel (112.36 mg/g) [5], peanut husk (37.5 mg/g) [4], peanut hull (87.72 mg/g) [3], and rice husk (32.37 mg/g) [15]. Compared to these adsorbents, the value of q_{max} for NR adsorption onto SCHS is much higher. Therefore, these values indicate that untreated SCHS seems to be more competitive than other low-cost NR biosorbents.
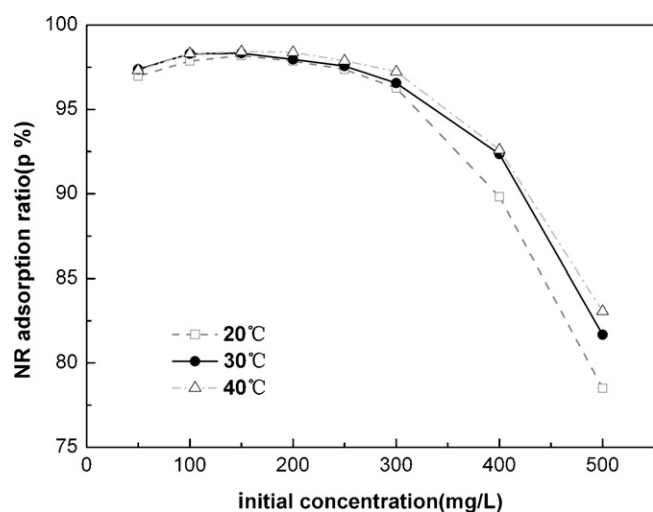

Fig. 6. Langmuir and Freundlich adsorption isotherms of NR on SCHS: (a) 20 °C; (b) 30 °C; (c) 40 °C.

Fig. 5. Equilibrium adsorption quantity of NR at different initial concentrations (reaction time 240 min, SCHS dosage 2.5 g/L, and pH 7.0).
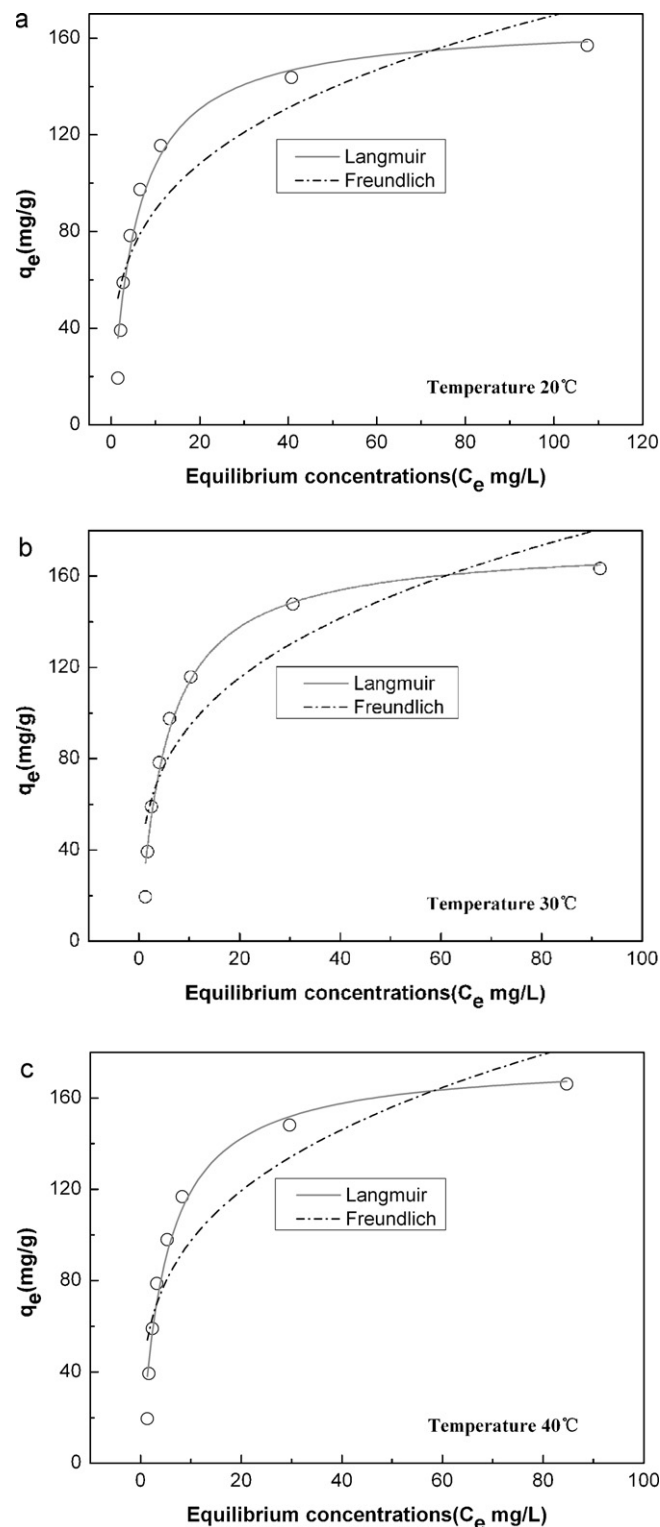
Table 3
Thermodynamic parameters calculated from Langmuir constant (K_L) for NR adsorption onto SCHS.

Temperature (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol K)
293	−29.50	4.67	0.1165
303	−30.57		
313	−31.83		

3.6. Adsorption thermodynamics

The amount of NR adsorbed onto SCHS at equilibrium at different temperatures was examined to obtain thermodynamic parameters. Changes in the free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were evaluated using the following equations [16–18] and can be calculated from a plot of ΔG° against T (Temperature, K) (Table 3):

$$\Delta G^\circ = -RT \ln(10^6 K_L) \tag{1}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{2}$$

where K_L is Langmuir constant when concentration terms are expressed in L/mg, R (8.314 J/mol K) is the universal gas constant.

As can be seen from Table 3, the positive value of ΔH° confirms the endothermic character of NR biosorption whereas the negative values of ΔG° indicate the spontaneity and feasibility of biosorption process. The decrease in ΔG° values with increasing temperature reveals that adsorption of NR onto SCHS becomes more favorable at higher temperature. Low value of ΔS° indicates that there is no remarkable change on entropy associated with the biosorption and the positive ΔS° values reflect affinity of the adsorbent for NR.

4. Conclusions

This study showed that SCHS could effectively remove NR dye from aqueous solution. The optimal pH for favorable adsorption of the dye was 4 and above. The percentage of dye adsorbed increased and reached a maximum value as the biosorbent dose increased. The kinetics of NR adsorption onto SCHS followed the pseudo-second order rate kinetics model. The equilibrium data fitted very well in a Langmuir isotherm equation according to the nonlinear curve fitting regressive analysis. The negative values of ΔG° and positive value of ΔH° showed that the adsorption was a spontaneous and endothermic process. Likewise, FTIR was employed for the characterization of the biosorbent. Therefore, SCHS can be used as a biosorbent for the removal of NR from its aqueous solution, without any laborious pretreatment steps before application.

Acknowledgements

References

[1] B.H. Hameed, Removal of cationic dye from aqueous solution using jackfruit peel as non-conventional low-cost adsorbent, J. Hazard. Mater. 162 (2009) 344–350.
[2] S.B. Wang, Z.H. Zhu, A. Coomes, F. Haghseresht, G.Q. Lu, The physical and surface chemical characteristics of activated carbons and the adsorption of methylene blue from wastewater, J. Colloid Interface Sci. 284 (2005) 440–446.
[3] R.M. Gong, M. Li, C. Yang, Y.Z. Sun, J. Chen, Removal of cationic dyes from aqueous solution by adsorption on peanut hull, J. Hazard. Mater. 121 (2005) 247–250.
[4] R. Han, P. Han, Z. Cai, Z. Zhao, M. Tang, Kinetics and isotherms of Neutral Red adsorption on peanut husk, J. Environ. Sci. 20 (2008) 1035–1041.
[5] R.M. Gong, X.P. Zhang, H.J. Liu, Y.Z. Sun, B.R. Liu, Uptake of cationic dyes from aqueous solution by biosorption onto granular kohlrabi peel, Bioresour. Technol. 98 (2007) 1319–1323.
[6] A.E. Rodriguez Estrada, D.J. Royse, Yield, size and bacterial blotch resistance of *Pleurotus eryngii* grown on cottonseed hulls/oak sawdust supplemented with manganese, copper and whole ground soybean, Bioresour. Technol. 98 (2007) 1898–1906.
[7] S. Akar, A. Gorgulu, Z. Kaynak, B. Anilan, T. Akar, Biosorption of Reactive Blue 49 dye under batch and continuous mode using a mixed biosorbent of macrofungus *Agaricus bisporus* and *Thuja orientalis* cones, Chem. Eng. J. 148 (2009) 26–34.
[8] G. Bayramoglu, G. Celik, M.Y. Arica, Biosorption of Reactive Blue 4 dye by native and treated fungus *Phanerocheate chrysosporium*: batch and continuous flow system studies, J. Hazard. Mater. 137 (2006) 1689–1697.
[9] M. Iqbal, A. Saeed, S.I. Zafar, FTIR spectrophotometry, kinetics and adsorption isotherms modeling, ion exchange, and EDX analysis for understanding the mechanism of Cd(2+) and Pb(2+) removal by mango peel waste, J. Hazard. Mater. 164 (2009) 161–171.
[10] T. Akar, B. Anilan, A. Gorgulu, S.T. Akar, Assessment of cationic dye biosorption characteristics of untreated and non-conventional biomass: *Pyracantha coccinea* berries, J. Hazard. Mater. 168 (2009) 1302–1309.
[11] G.Q. Chen, G.M. Zeng, X. Tu, G.H. Huang, Y.N. Chen, A novel biosorbent: characterization of the spent mushroom compost and its application for removal of heavy metals, J. Environ. Sci. 17 (2005) 756–760.
[12] A. Sari, M. Tuzen, Kinetic and equilibrium studies of biosorption of Pb(II) and Cd(II) from aqueous solution by macrofungus (*Amanita rubescens*) biomass, J. Hazard. Mater. 164 (2009) 1004–1011.
[13] N. Nasuha, B.H. Hameed, A.T.M. Din, Rejected tea as a potential low-cost adsorbent for the removal of methylene blue, J. Hazard. Mater. 175 (2000) 126–132.
[14] B.H. Hameed, Grass waste: a novel sorbent for the removal of basic dye from aqueous solution, J. Hazard. Mater. 166 (2009) 233–238.
[15] W.H. Zou, P. Han, Y.L. Lia, X. Liu, X.T. He, R.P. Han, Equilibrium, kinetic and mechanism study for the adsorption of Neutral Red onto rice husk, Desalination Water Treat. 12 (2009) 210–218.
[16] P. Luo, Y. Zhao, B. Zhang, J. Liu, Y. Yang, Study on the adsorption of Neutral Red from aqueous solution onto halloysite nanotubes, Water Res. 44 (2010) 1489–1497.
[17] T. Akar, I. Tosun, Z. Kaynak, E. Kavas, G. Incirkus, S.T. Akar, Assessment of the biosorption characteristics of a macro-fungus for the decolorization of Acid Red 44 (AR44) dye, J. Hazard. Mater. 171 (2009) 865–871.
[18] S.K. Milonjic, A consideration of the correct calculation of thermodynamic parameters of adsorption, J. Serb. Chem. Soc. 72 (2007) 1363–1367.