THE REMOVAL OF REACTIVE RED 228 DYE FROM AQUEOUS SOLUTIONS BY CHITOSAN-MODIFIED FLAX SHIVE

Hao Feng, Jian Li, and Lijuan Wang*

Flax shive (FS) is a byproduct from flax fiber separation. The use of absorbent prepared from chitosan-modified flax shive (CFS) has been studied for removal of reactive red dye (RR228) from aqueous solutions. CFS was characterized by the Brunauer-Emmett-Teller (BET) method, Scanning Electron Microscopy (SEM), Fourier Transform Infrared spectrometry (FTIR), and X-ray photoelectron spectroscopy (XPS). A batch adsorption study was conducted under various contact time, initial concentration, solution pH, and adsorbent dosage. It was found that the BET and Langmuir surface area of CFS were 1.772 $m^2 g^{-1}$ and 3.057 $m^2 g^{-1}$, respectively. Results showed that CFS has the same pores as FS and that the $-NH_2$ group on CFS is the main adsorption site for dye sorption. Equilibrium adsorption capacity could be reached within 480 min, and RR228 uptake was satisfactory at a pH of 2.0. The percentage removal were 100%, 100%, 90%, and 85% at pH 2.0 under dye concentrations of 10 mg/L, 20 mg/L, 30 mg/L, and 40 mg/L, respectively. The adsorption accurately fitted a pseudo-second-order kinetic model and a Langmuir isotherm model. It is proposed that CFS could be applied as a low-cost absorbent in removal of dyes from wastewater.

Keywords: Adsorption; Reactive red 228; Chitosan-modified flax shive; Kinetics; Isotherms

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INTRODUCTION

Dyes are widely utilized in many industries including textiles, paper, leather, plastic, food, painting, etc. (Altınışık et al. 2010; Safa et al. 2011). They can color various products to offer a sense of beauty. However, the waste water from the industries involving dye still contains up to 10% of dye (Moussavi et al. 2011). The presence of a small amount of dye in water is highly visible and harmful. Dyes are synthetic organic compounds, and most of them are toxic and even carcinogenic (Crini 2008). Also, they are usually stable and difficult to resolve into innocuous substances (El Ashtoukhy 2009). Therefore, industrial effluents containing dyes are hazardous and can cause fatal harm to animals and plants. Thus, it is necessary to remove dyes from industrial effluents.

Some methods can be used in removing dyes from waste water, such as membrane filtration, electro-coagulation, electrochemical destruction, ion-exchange, irradiation, advanced oxidation, precipitation, and adsorption (Jain et al. 2008). However, most of those processes involve high cost and low efficiency.

Adsorption has been found to be a very effective process for most pollutant removal from industrial effluents. Activated carbon (AC) has shown excellent performance in adsorption (Baccar et al. 2009). However, it is too expensive and difficult to regenerate (Mahmoodi et al. 2011a). In the past few years, more and more attention has been paid to low-cost absorbents for wastewater treatment. Agricultural wastes (Bhattacharyya et al. 2005; McKay et al. 1986; Namasivayam et al. 1996; Namasivayam et al. 1998) and by-products (Batzias et al. 2007; Hamdaoui et al. 2006; Jain et al. 2010; Kumar et al. 2007; Waranusantigul et al. 2003) have been studied in detail for the removal of dyes from aqueous solution. However, many low-cost absorbents have relatively low adsorption capacity; therefore, the consumption amounts are very huge. At present, the key studies are focused on finding new and economical adsorbents or improving adsorption capacity of those low-cost absorbents.

Flax is planted worldwide, mainly for producing fiber and seed oil (Sankari 2000). Flax shive (FS) is from the woody part of the straw and the main by-product in fiber separation by retting. FS is a kind of natural material consisting of cellulose and lignin. The content of each component is close to that of poplar wood. About 2.5 tons of shives are produced in the course of separating each ton of fiber. In North America, the amount of FS can be estimated at 2.1 million tones annually. And the amount in China is about 1.0 million tons. FS is traditionally used as a waste in some low-value applications such as burning for thermal energy, animal bedding, and particle-board. In recent years, it has been used as training material for edible mushroom production. Researchers (Cox et al. 1999, 2000; El-Shafey et al. 2002) have studied the carbonaceous material from flax shive by sulfuric acid treatment. Cellulose was separated from FS and synthesized super water absorbent (Feng et al. 2010). Recently, FS has been applied as bio-absorbent to absorb metal ions. However, up to the best of our knowledge, there has been no paper reporting the use of FS for dye removal from aqueous effluents.

Chitosan is a kind of natural polymer derived from chitin; it is considered to be an environmentally friendly raw material, as it is biodegradable and non-toxic. It is widely used in many fields, such as food processing, medicine, biochemistry, textiles, biotechnology, agriculture, and wastewater treatment (Guibal et al. 2005; Pillai et al. 2009; Rani et al. 2010). Recent studies have indicated that chitosan has become one of the most popular absorbents for removing dyes and metal ions from aqueous solutions. It can be also used to modify some absorbents to improve their absorption capacities.

In this study, chitosan-modified flax shive (CFS) powders have been used for active red dye removal from aqueous solution at various conditions. Kinetic and isotherm parameters also are discussed.

EXPERIMENTAL

Preparation of Adsorbent

FS was obtained from a local flax mill. It was washed about 5 times with tap water to remove dust and dried in sunlight for about 5 days. Then they were ground with a high-speed grinder to obtain powders of 80 to 100 mesh. The powder was cooked in distilled water for 1 hour to remove soluble components. The cooked powder was designated as un-modified absorbent. 50 gram of cooked powders, 50 mL of chitosan solution with concentration of 1 wt% volume, and 7.5 mL of glycerol were mixed and agitated for 1 hour, filtered, then dried at 100 ^oC for 30 min and 160 ^oC for 10 min. The dried material was ground and stored in a plastic bag for further use.

The chemical scheme of the modification is shown in Fig. 1. Glycerol cross-linked chitosan formed in the membrane and ether bonds formed between chitosan and cellulose molecules on the interface under acid condition and high temperature.

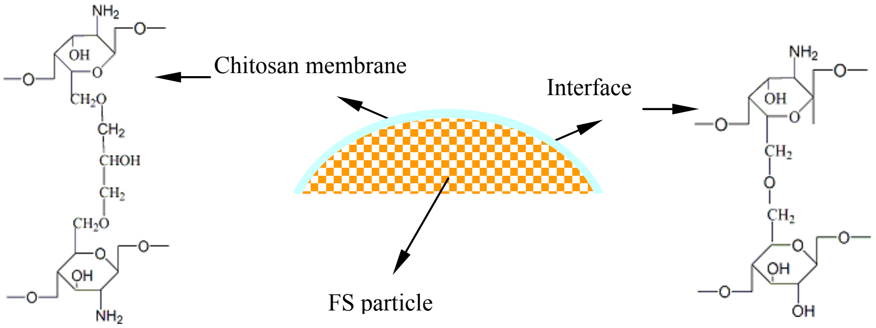

Fig. 1. Chemical scheme of chitosan modification of FS

Preparation of Dye Solution

Reactive red dye (C.I. Reactive Red 228, λ_{max} 510 nm) was used in this study. The structure is shown in Fig. 2. It was obtained from Ciba Company. An accurate weighed quantity of the dye was dissolved in distilled water to prepare stock solution (100 mg/L). Experimental solutions of various concentrations were obtained by further dilutions. Standard curves were developed via the absorbance measurement of the dye solution by UV-Visible spectrophotometer (TU-1900).

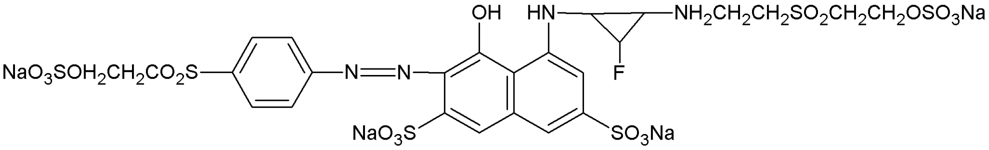

Fig. 2. Structure of reactive red dye (C.I. Reactive red 228)

Adsorption Experiment

Adsorption experiments were conducted in batch mode to evaluate the effects of various parameters such as pH, adsorbent dose, initial dye concentration, and contact time on the adsorption of RR228. In each adsorption experiment, 100 mL of dye solution was added to the amount of absorbent in a 250 mL of conical flask at room temperature, and the mixture was shaken on a shaker at 190 rpm.

The sample was withdrawn from the shaker at the end of the adsorption, and the adsorbents were separated from the solution with a nylon screen with pore size of 400 mesh. The absorbance of the residue solution was measured to enable calculation of the dye concentration.

The amount of absorbed dye per unit mass was calculated by using the following equation,

$$q_e = (C_0\text{-}C_e)V/W \qquad (1)$$

where q is the amount of dye absorbed on the absorbent (mg/g), and C_0 and C_e (mg/L) are the initial and equilibrium concentration of dye solution, respectively. V is the volume of dye solution (mL), and W is the amount of the absorbent (g).

The percentages of RR228 removal were calculated based on the equation below,

$$\%\text{ of RR228 removal} = (C_0\text{-}C_i)/C_0 \times 100\% \qquad (2)$$

where C_i is the dye concentration at a given moment, and other quantities are the same as those mentioned above.

The effect of pH on adsorption of RR228 onto CFS was adjusted at different pH values (2 to 10) by adding a few drops of NaOH or HCl solution.

Kinetic Studies

Kinetics of adsorption was determined by analyzing the dye absorbed from aqueous solution at different time intervals. Initial dye concentration in the test solution and adsorbent dosage were varied to investigate their effects on the adsorption kinetics.

Characterization

FTIR spectra were recorded using a Nicolet 560 spectrometer (Nicolet Co., USA) at a resolution of 4 cm and using the KBr pellet method. Morphological analysis was conducted with a Quanta 200 device, Philips-FEI Co., The Netherlands. The scanned surfaces were coated with a thin layer of gold before observation. The nitrogen sorption isotherms were measured by volumetric method on an automatic adsorption instrument (ASAP2020, USA) at liquid nitrogen temperature (77.2 K). Specific surface area was calculated by the Nrumauer-Emmett-Teller (BET) method from the data in a P/P_0 range of 0.06-0.2.

RESULTS AND DISCUSSION

Characterization of the Absorbents

Table 1 shows the characteristics of CFS. The porosity was not ideal, and the surface area was relatively low. In the FTIR spectrum (Fig. 3), a broad absorption peak was observed at 3416 cm^{-1}, which is attributed to the vibration of –OH groups and $–NH_2$ groups. Two peaks at around 2932 cm^{-1} and 2884 cm^{-1} correspond to the stretching vibration of the methylene. The peaks at 1640 cm^{-1} and 1737 cm^{-1} correspond to –C=O bonds and the carboxyl absorption. The peak at 1465 cm^{-1} is ascribed to aromatic groups. The peak at around 1060 cm^{-1} is the characteristic peak of the pyranoid ring in cellulose and chitosan. These groups on the CSF surface are $–NH_2$, -OH, -COOH, etc. It is believed that $–NH_2$ is the main adsorption site for dye RR228. This statement is further proved by N1s XPS analysis (Fig. 4). In Fig. 4(a), two peaks at 398.28eV and 399.88ev are attributed –NH_2 group and –NH_3^+ group, which indicates that part of the –NH_2 groups on chitosan changed to the –NH_3^+ form in acetic acid solution in the dissolving and modification process.

Table 1. Characteristics of CFS

BET surface area (cm^3/g)	Langmuir surface area(cm^3/g)	Pore size (nm)	pH_{PZC}	Bulk density (g/cm^3)
1.772	3.057	6.219	~1.99	0.261

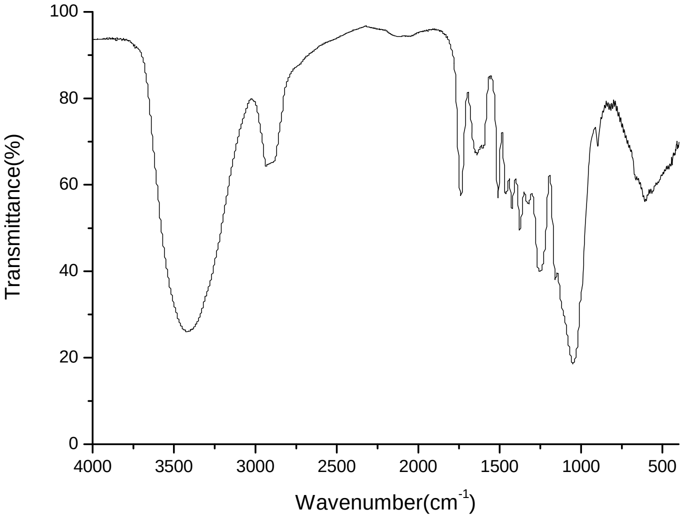

Fig. 3. FTIR spectrum of CFS

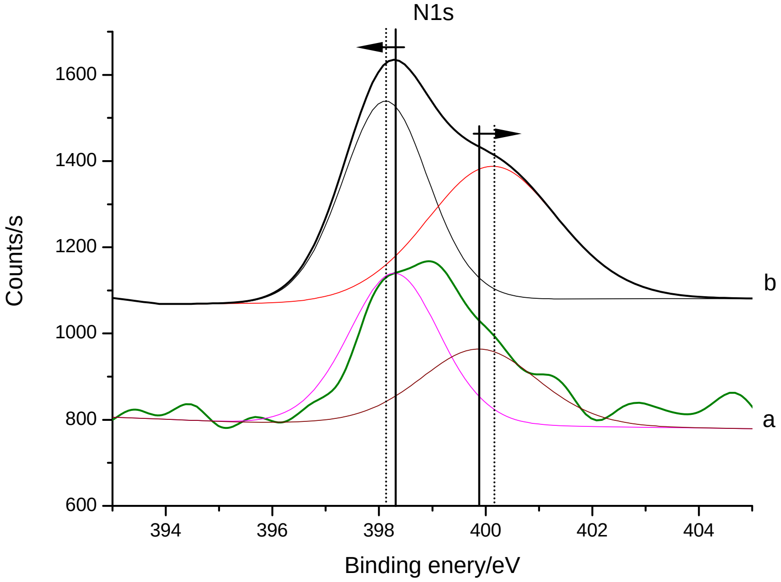

Fig. 4. N1s XPS spectra of (a) CFS, and (b) CFS loaded RR228 (adsorption under pH=2)

After RR228 adsorption, as shown in Fig. 4(b), the peak corresponding to the $–NH_3^+$ group became stronger and was shifted from 399.88 to 400.18eV, indicating that other $–NH_2$ groups on chitosan also were transformed to $–NH_3^+$ during the adsorption at a pH value of 2, and the adsorption of dye molecules makes the peak shift to higher binding energy. The peak associated with the $–NH_2$ group at 398.1eV became stronger because the absorbed dye molecules contain some $–NH_2$ groups and some –NH– groups.

The morphologies of CFS particles are shown in Fig. 5. FC is the woody part of the flax straw and characterized by ordered rows of tubular structures. CFS kept the originally porous structures after chitosan treatment.

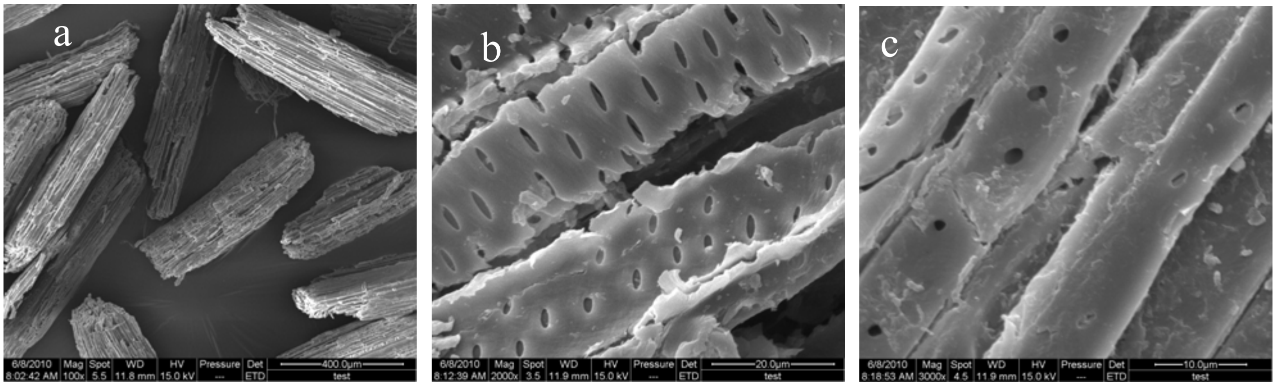

Fig. 5. SEM photographs of CFS particles in magnification of (b) 100 times, (c) 2000 times, and (d) 3000 times

Adsorption of RR228 on FS Before and After Modification

Figure 6 compares the adsorption capacity of RR228 on FS and CFS. With the contact time increasing, the adsorption capacity increased and reached 8.87 mg/g and 0.45 mg/g at a contact time of 480 min. CFS exhibited obviously higher adsorption capacity than FS.

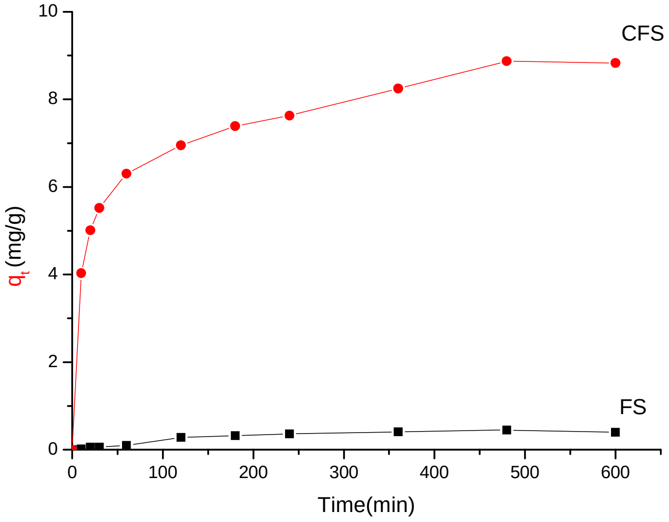

Fig. 6. Adsorption capacities of FS and CFS (RR228 conc. 10mg L^{-1}, FS and CFS dosage 1 g L^{-1})

Effect of Contact Time and Initial Dye Concentration

The effects of contact time and initial concentration on adsorption of RR228 on CFS were investigated, and the results are shown in Fig. 7 (a). The shaking time was varied from 0 to 600 min, and the initial dye concentration was in the range from 10 to 40 mg/L. The extent of the adsorption was found to increase with increase in contact time. When the contact time was fixed, the effect of initial concentration on adsorption capacity could be easily observed as an increase in the adsorption capacity; however, the magnitude of the increase became smaller with increasing initial dye concentration. As shown in Fig. 7 (b), the efficiency of dye removal was very high for lower initial dye concentration.

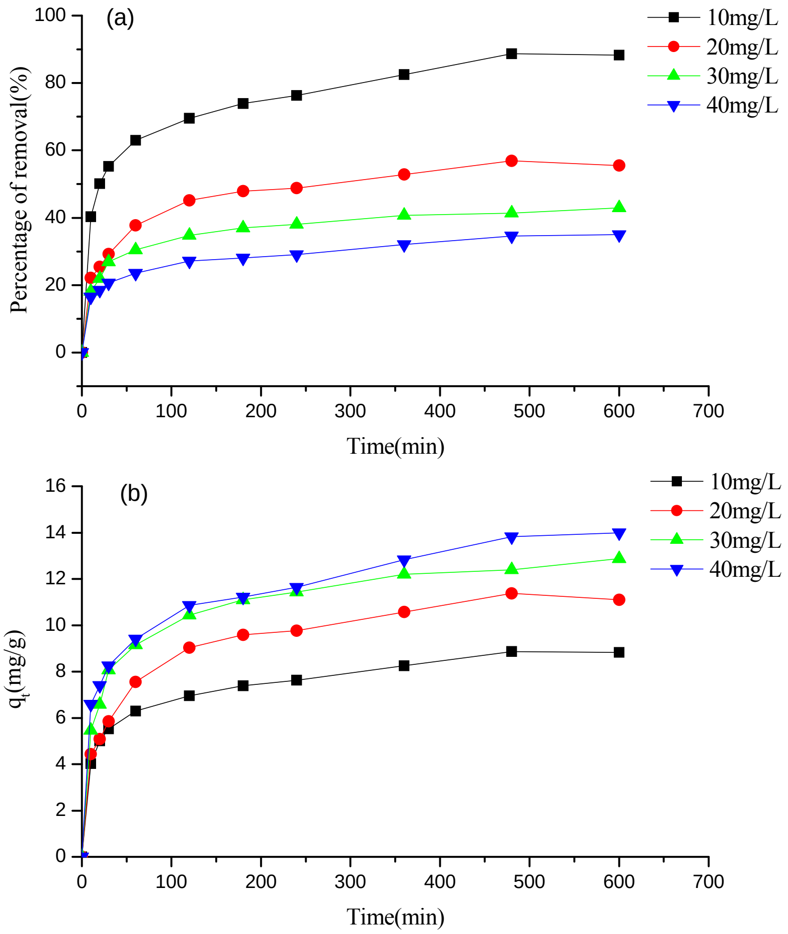

Fig. 7. The influence of RR228 concentration on removal and adsorption capacity by CFS(RR228 concentration 10mg L^{-1}, CFS dosage 1 g L^{-1})

The effects of contact time and initial concentration on adsorption of RR228 on commercial activated carbon were also investigated. The results in Fig. 8 indicate that RR228 was quickly absorbed on the activated carbon and reached the equilibrium in shorter time. Comparing the absorption capacity of the two absorbents, it was found that the capacity of the activated carbon was about two times of that of CFS under the same initial concentration and contact time. Based on an overall consideration of various factors, it is significant to utilize CFS to remove RR228 from aqueous solution instead of activated carbon.

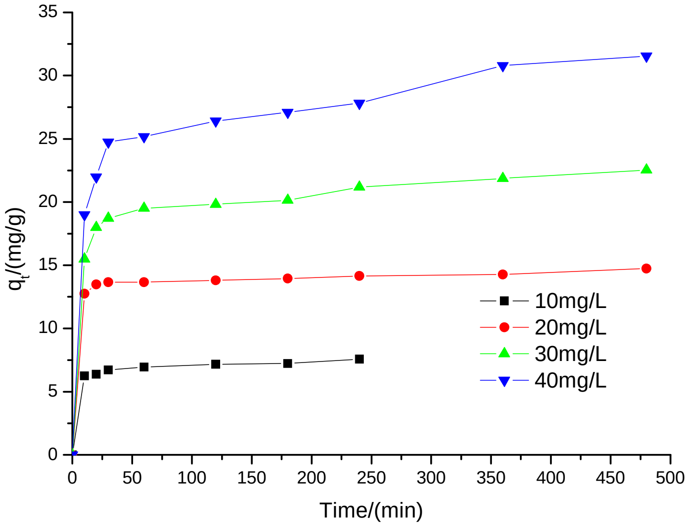

Fig. 8. The influence of RR228 concentration on adsorption capacity by commercial activated carbon(RR228 concentration 10mg L^{-1}, CFS dosage 1 g L^{-1})

The Effect of Initial pH of Dye Solution

The pH of the dye solution is an important variable for the adsorption. The effects of pH on the absorption of RR228 on CFS were studied in the pH range from 2 to 10, and results are shown in Fig. 9.

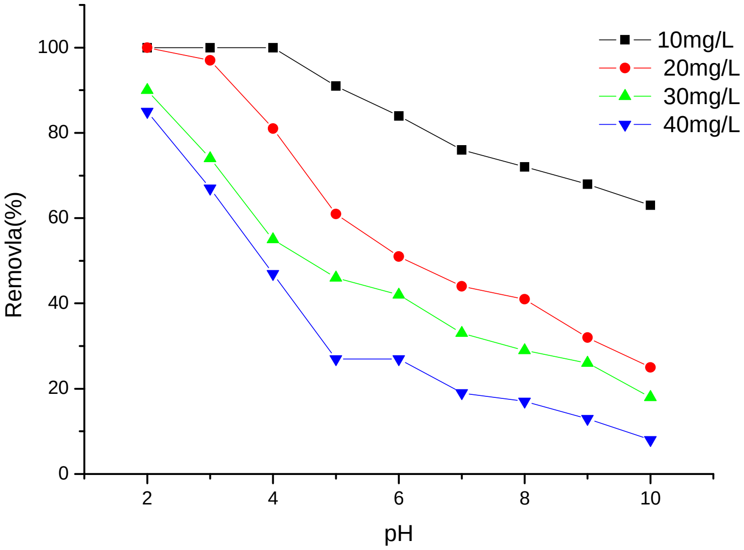

Fig. 9. Influence of solution pH on absorption of RR228 by CSF (RR228 concentration 10mg L^{-1}, CFS dosage 1 g L^{-1})

The maximum absorption was at pH 2.0. However, the absorption was not effective at higher pH values. The removal rate decreased from 100%, 100%, 90%, and 85% at pH 2.0 to 63%, 25%, 18%, and 8% at pH 10 at dye concentrations of 10 mg/L, 20 mg/L, 30 mg/L, and 40 mg/L, respectively. It is known that the chitosan molecular contains the amine group (-NH_2), which is easily protonated to form –NH_3^+ in acidic solution (Mahmoodi et al. 2011b). As shown in Fig. 10, the higher removal is due to the strong electrostatic interaction between the –NH_3^+ of chitosan and anions (-SO_3^-) of the dye RR228. Certainly, the lower removal rate at higher pH values is attributed to the lack of interaction between the -NH_2 and anions in the dye. Therefore, the optimum pH value for the adsorption is around 2.

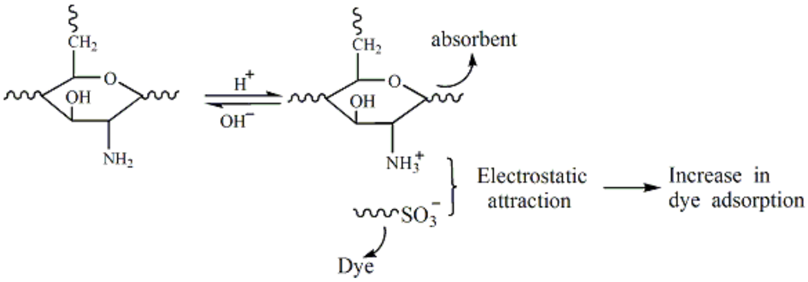

Fig. 10. Schematics of the adsorption of RR228 on CFS

The Effect of Absorbent Dosage

Figure 11 shows the adsorption of dye RR228 onto the CFS for different adsorbent dose (0 to 0.5g/100mL) at different initial dye concentrations. It was observed that the removal rate of dye RR228 increased with the increased in CFS dose.

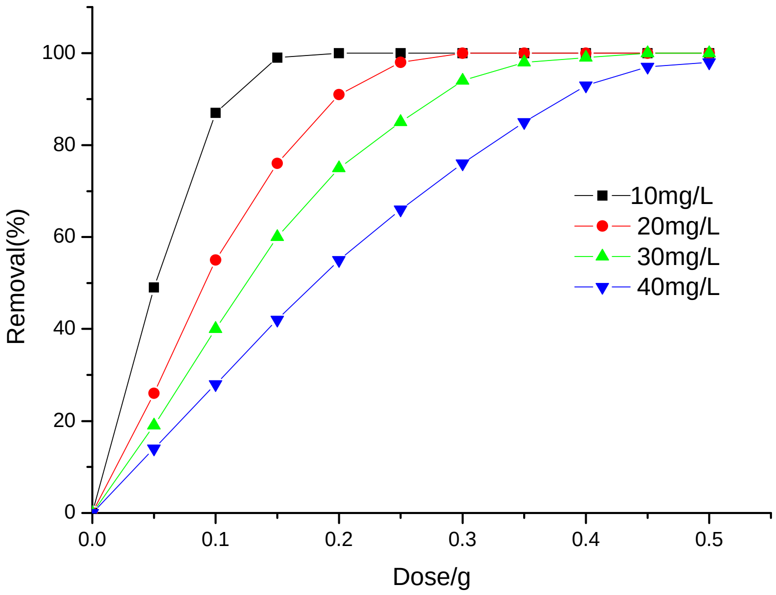

Fig. 11. Influence of CFS dosage on RR228 removal under different solution concentration

However, the removal rate decreased with the increased in dye concentration under the same dose of CFS. The higher removal at high dosage of absorbent may be due to the more binding sites for the dye. 100% removal was observed at a CFS dosage of 0.15 g, 0.2 g, 0.35 g, and 0.5 g at solution concentrations of 10 mg/L, 20 mg/L, 30 mg/L, and 40 mg/L, respectively.

Adsorption Kinetics

Study of kinetics is important to optimize different operating parameters for the sorption process. Three kinetic models have been suggested in order to explain the order of the adsorption.

The kinetics of RR228 sorption onto CFS was analyzed using pseudo-first order, pseudo-second order, and intraparticle diffusion kinetic models.

Pseudo-first order kinetic model

The pseudo-first order kinetic model (Ahmad et al 2007) can be expressed as follows,

$$dq_t/dt=k_1(q_e-q_t) \tag{3}$$

where q_e and q_t are the adsorption capacity (mg/g) at equilibrium and time t, respectively. k_1 is the rate constant (L min^{-1}) of pseudo-first order kinetic model.

After integrating and rearranging Eq. 3, the linear form is obtained, as below:

$$\ln(q_e-q_t) = \ln q_e - k_1 t \tag{4}$$

Straight-line plots of $\log(q_e-q_t)$ against t (Eq. 4) were made at different dye concentrations, as shown in Fig. 12.

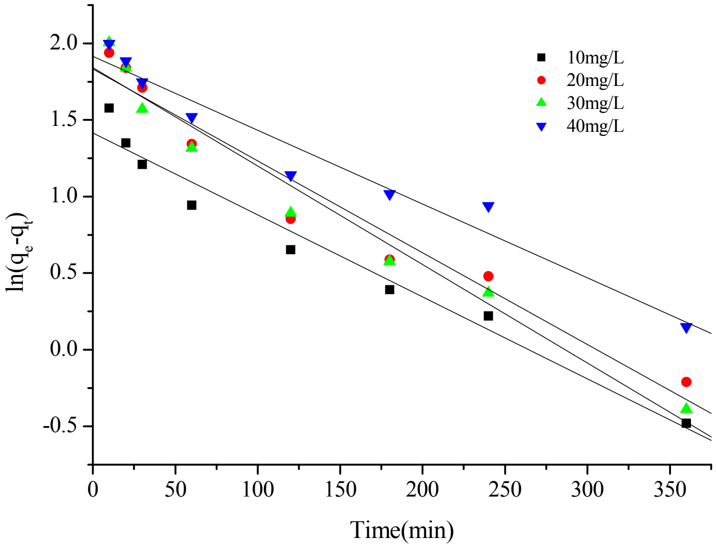

Fig. 12. Pseudo-first-order plots of absorption of different concentrations of RR228 on CFS

Values of the rate constant k_1, q_e,exp, q_e,calc, and R^2 of RR228 are presented in Table 2. It is shown that the values of R^2 were satisfactory; however, the value of q_e,calc was only about half that of q_e,exp. Therefore, the adsorption did not fit the pseudo-first order kinetic model well.

Pseudo-second order

The pseudo-second order kinetic model (Katuri et al 2009) can be expressed as follows,

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

where k_2 (g mg^{-1} min^{-1}) is the rate constant for the pseudo-second order kinetic model. The q_e and k_2 values were estimated from the slope ($1/q_e$) and intercept ($1/k_2 q_e^2$) of a linear plot of t/q_t versus t at different dye concentrations.

The second-order linear plots and parameters k_2, q_e,exp, q_e,calc, and R^2 of RR228 are shown in Fig. 13 and Table 2. It is indicated that q_e,calc and q_e,exp were very close and all the values of R^2 were higher than 0.99, which showed that the adsorption of RR228 on CFS accurately followed the pseudo-second order kinetic model.

Intraparticle diffusion model

The intraparticle diffusion model is based on the transfer of matter from the exterior of a substrate surface to internal surfaces of the pores, which is generally considered to involve three consecutive steps:

① Transport of absorbate molecules from the bulk solution to the adsorbent external surface through the boundary layer diffusion;

② Diffusion of the adsorbate from the external surface into the pores of the adsorbent; and

③ Adsorption of the adsorbate on the active sites on the internal surface of the pores (Cheung et al 2007). The intraparticcle diffusion model is given by the following equation,

$$q_t = k_{pi} t^{0.5} \tag{6}$$

where q_t is the amount adsorbed (mg/g) at time t.

As seen in Fig. 14, the straight lines did not pass through the origin, and this indicated that more than one process affected the adsorption but only one was rate-limiting in any particular time range (Li et al. 2007; Zhong et al. 2011). The slope of the linear portion reflected the rate of the adsorption. As shown in Table 2, the slope decreased from the first portion to the third portion. This implied that the intraparticle diffusion of RR228 molecular into micropores was the rate-limiting step in the adsorption process on CFS.

In short, the pseudo-second order kinetic model is most suitable for the adsorption of RR228 on CFS.

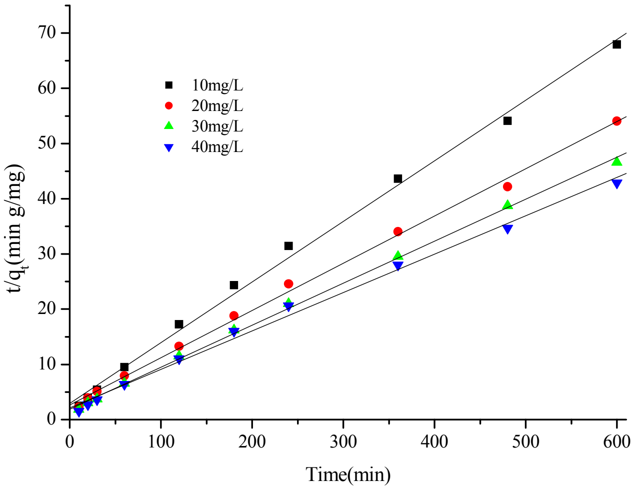

Fig. 13. Pseudo-second-order plots of absorption of different concentrations of RR228 on CFS

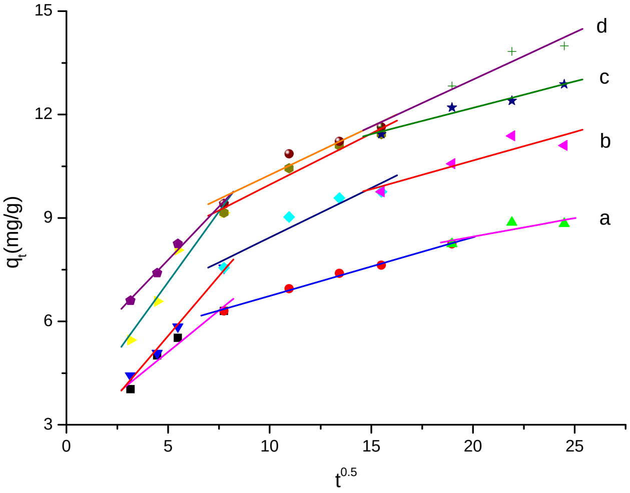

Fig. 14. Plots of intraparticle diffusion model of adsorption of different concentrations (a) 10mg/L, (b)20mg/L, (c)30mg/L, and (d) 40mg/L of RR228 on CFS

Adsorption Isotherm

Several models have been used to describe experimental data of adsorption isotherms. The Langmuir and Freundlich are the most often-used models. The Langmuir isotherm is based on a hypothesis that uptake occurs on a homogeneous surface by monolayer adsorption without interaction between the absorbed materials (Li et al. 2009). The application of Langmuir model to the experiment equilibrium isotherm data for RR228 adsorption by CFS produces two parameters: the maximum adsorption capacity q_m (mg g^{-1}) and the constant b (L mg $^{-1}$). The linear equation can be expressed as below:

$$C_e/q_e=1/(bq_m) + C_e/q_m \quad (7)$$

It is a dimensionless separation factor used to determine if the adsorption process is favorable or unfavorable. The shapes of the isotherms for $0< R_L <1$, $R_L >1$, $R_L=1$, $R_L=0$ are favorable, unfavorable, linear and irreversible, respectively.

$$R_L=1/(1+a_LC_0) \tag{8}$$

Table 2. Kinetic Parameters for the Adsorption of RR228 on CFS

Kinetic models	Initial concentration of dye solution(mg/L)			
	10	20	30	40
Pseudo-first order				
k_1 (min^{-1})	0.0054	0.0060	0.0064	0.0048
q_e, calc (mg g^{-1})	4.12	6.25	6.31	6.79
R^2	0.969	0.956	0.968	0.960
Pseudo-second order				
k_2 (mg g^{-1} min^{-1})	0.0041	0.0028	0.0031	0.0023
q_e, exp (mg g^{-1})	8.87	11.38	12.88	13.99
q_e, calc (mg g^{-1})	9.11	11.68	13.14	14.37
R^2	0.996	0.998	0.999	0.994
Intraparticle diffusion				
k_{p1} (mg g^{-1} min$^{-1/2}$)	0.4807	0.6919	0.8170	0.6177
R^2	0.979	0.996	0.975	0.995
k_{p2} (mg g^{-1} min$^{-1/2}$)	0.1705	0.2881	0.2974	0.2810
R^2	0.997	0.958	0.983	0.967
k_{p3} (mg g^{-1} min$^{-1/2}$)	0.1075	0.1658	0.1529	0.2727
R^2	0.856	0.902	0.982	0.974

The Freundlich isotherm is commonly used for investigating non-linear adsorption of a variety of dyes on various materials. The Freundlich isotherm (Freundlich 1906) is given by the following equation,

$$q_e=k_fC_e^{1/n} \tag{9}$$

where k_f (mg g^{-1}) is coefficient for the adsorbed amount and n is the Freundlich constant.

The adsorption data were also found to fit the linear form of the Freundlich equation:

$$\log q_e =\log k_f +(1/n)\log C_e \tag{10}$$

Table 3 shows the calculated parameters for Langmuir and Freundich isotherms models for RR228 on CFS. R^2 values were 0.994 and 0.988, respectively. This indicates that the adsorption of RR228 on CFS obeyed the Langmuir model well compared to Freundlich isotherms. This result suggests that the uptake of RR228 occurs on a homogeneous surface of CFS by monolayer adsorption without interaction between the absorbed RR228 molecules. The R_L value was 0.036 in the range of 0 to 1, which shows that the adsorption was favorable.

Table 3. Calculated Parameters for Langmuir and Freundich Isotherm Models for RR228 on CFS

Langmuir isotherm

b(L mg^{-1})	q_m(mg g^{-1})	R_L	R^2
0.67	14.45	0.036	0.994

Freundich isotherm

n	K_f (mg g^{-1})	R^2
0.141	8.65	0.988

CONCLUSIONS

1. The adsorption capacity of RR228 on FS was significantly increased by chitosan modification.
2. CFS kept the porous structure of FS. The BET and Langmuir surface area of CFS were found to be 1.278 and 3.057 m^2 g^{-1}, respectively. –NH$_2$ groups on CFS are the main adsorption sites for dye RR228.
3. Contact time, initial concentration, solution pH, and adsorbent dosage obviously affect the adsorption capacity of CFS.
4. The kinetic study indicated parameters of RR228 adsorption onto CFS absorbent followed the pseudo-second-order model better than the pseudo-first-order model. Intraparticle diffusion analysis showed that that the intraparticle diffusion of RR228 molecular into micropores was the rate-limiting step in the adsorption process on CFS.
5. Parameters from isotherm study indicate that the equilibrium data were well fitted to the Langmuir isotherm model, which implied monolayer adsorption of RR228 on CFS. The maximum adsorption capacity was 14.43 mg/g.

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