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Preparation and utilization of rice straw bearing carboxyl groups for removal of basic dyes from aqueous solution

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Abstract

One kind of potentially biodegradable cationic sorbent with high sorption capacity of basic dyes was prepared by thermochemically esterifying oxalic acid onto rice straw, and then the esterified rice straw was further loaded with sodium ion for enhancing its cationic sorption capacity. The sorption of two basic dyes, basic blue 9 (BB9) and basic green 4 (BG4), from aqueous solutions onto modified product was investigated. The effects of various experimental parameters (e.g. initial pH, sorbent dosage, dye concentration, ion strength, contact time) were examined and optimal experimental conditions were decided. The BB9 and BG4 removal ratios came up to the maximum value beyond pH 6. The 2.0 g/l or above of sorbent could almost completely remove BB9 and BG4 from 250 mg/l of dye solution. The ratios of BB9 and BG4 sorbed kept above 97% over a range from 50 to 250 mg/l of dye concentration when 2.0 g/l of sorbent was used. Increase in ion strength of solution induced decline of BB9 and BG4 sorption. The isothermal data fitted well to the Langmuir and Freundlich models. The sorption processes could be described by the pseudo-second-order kinetic model. The results in this research confirmed that the OA-modified rice straw was an excellent basic dye sorbent.

Keywords: Sorption; Basic blue 9; Basic green 4; Thermochemical esterification; Oxalic acid; Rice straw

1. Introduction

Dyes are a kind of synthetic aromatic compounds which can be used to impart color to other materials. The complex aromatic molecular structures of dyes usually come from coal-tar based hydrocarbons such as benzene, naphthalene, anthracene, toluene and xylene. Today there are more than 10,000 dyes with different chemical structures available commercially and over 7×10^5 tons of these dyes are produced worldwide annually [1,2].

Dyes are important water pollutants which are generally present in the effluents of the textile, leather, paper, rubber, plastics, cosmetics, pharmaceuticals and foodstuff industries. Dye wastewater discharge into environmental water bodies deteriorates the water quality, and may cause a significant impact on human health due to mutagenic, teratogenic or carcinogenic effects of some dyes or their metabolites [3,4]. Due to water resource shortage and socio-economic development, China is facing serious problems of water supply and water pollution.

Some biological and physical/chemical methods have been employed for dye wastewater treatment [5–11]. In all these methods, the sorption has been found to be economical and effective dye wastewater treatment technology as it can remove various dyes with lower treatment cost.

Though the removal of dyes through sorption of activated carbon is quite effective, its use is restricted in developing countries like China sometimes due to the higher cost of activated carbon and difficulties associated with regeneration. Attempts have therefore been made to utilize natural as well as waste materials as alternative sorbents. Agricultural by-products are considered to be low value products. Because of low utilization

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ratio, most of these biomaterials are arbitrarily discarded or set on fire. These disposals must result in resource loss and environmental pollution. The exploitation and utilization of these biomaterials must bring obvious economic and social benefits to mankind. In recent years, some crude agricultural by-products have been investigated and utilized as sorbent, which included coconut husk [12], bagasse pith [13], palm-fruit bunch [14], eucalyptus bark [15], apple pomace and wheat straw [16], banana and orange peel [17], neem leaf [18], kudzu [19] and peanut hull [20]. Generally, sorption capacity of crude agricultural by-products is low. For improving the sorption capacity of crude agricultural by-products, various chemical modifications were employed [21–26].

Rice straw is a lignocellulosic agricultural by-product containing cellulose (37.4%), hemi-cellulose (44.9%), lignin (4.9%) and silicon ash (13.1%) [27]. In China, about 200 billion kg of rice straw are produced annually as a by-product of rice production. The smoke caused by open-field burning rice straw frequently results in serious air pollution and traffic trouble, hence new economical technologies for rice straw disposal and utilization must be developed. In this paper, rice straw was thermochemically esterified by oxalic acid (OA). The esterified rice straw was further loaded with sodium ion in order to yield potentially biodegradable cationic sorbent. The feasibility of the modified product as cationic dye sorbent for removing basic dyes from aqueous solution was investigated. The objective of this work was to develop a new economical technology for rice straw exploitation and utilization and to enhance the treatment of industrial wastewater and reduce the cost of wastewater treatment.

2. Materials and methods

2.1. Preparation of modified sorbent

Rice straw was collected from a local farm. The collected biomaterial was cut into segment of 10 cm length and washed with tap water to remove soil and dust, and then dried overnight at 50 °C. Dried straw segment was ground and sieved to retain the 20–40 mesh fractions for further chemical modification.

The thermochemical modification of rice straw was performed according to the similar method [28]. Ground rice straw was blent with 0.5 M OA at the ratio of 1:12 (straw:acid, w/v) and stirred for 30 min. The acid/straw slurry was placed in a stainless steel tray and dried at 50 °C in a forced air oven. After 24 h, the thermochemical esterification between acid and straw was proceeded by raising the oven temperature to 120 °C for 90 min. After cooling, the OA-modified rice straw was washed with distilled water until the liquid did not turn turbid when 0.1 M calcium(II) chloride was dropped in. After filtration, the OA-modified rice straw was suspended in 0.1 M NaOH at suitable ratio and stirred for 60 min, followed by washing thoroughly with distilled water to remove residual alkali, and then the wet OA-modified rice straw was dried at 50 °C for 24 h and preserved in a desiccator for further use as sorbent.

2.2. Preparation of basic dye solution

Two basic dyes in highest grade available, basic blue 9 (BB9) and basic green 4 (BG4), were used without further purification. BB9 is a basic dye of phenothiazine type (C.I. No. 52015, FW = 373.9, $\lambda_{max} = 670$ nm) and BG4 is a basic dye of triphenylmethane type (C.I. No. 42,000, FW = 364.9, $\lambda_{max} = 617$ nm). The dye stock solutions were prepared by dissolving accurately weighted dyes in distilled water to the concentration of 500 mg/l. The experimental solutions were obtained by diluting the dye stock solutions in accurate proportions to different initial concentrations.

2.3. Experimental methods and measurements

Sorption experiments were carried out in a rotary shaker at 150 rpm and ambient temperature (20 ± 2 °C) using 250 ml shaking flasks containing 100 ml different concentrations and initial pH values of dye solution. The initial pH values of the solution were previously adjusted with 0.1 M HNO_3 or NaOH using pH meter. Different doses of sorbent were added to each flask. After shaking the flasks for predetermined time intervals, the samples were withdrawn from the flasks and the dye solutions were separated from the sorbent by sedimentation/centrifugation. Dye concentrations in the supernatant solutions were estimated by measuring absorbance at maximum wavelengths of dyes with a 752W Grating Spectrophotometer (Shanghai, China) and computing from the calibration curves.

The experiments were conducted in duplicates and the negative controls (with no sorbent) were simultaneously carried out to ensure that sorption was by sorbent and not by the container.

2.4. IR spectra study

The IR spectra of rice straw before and after esterification were performed on a Fourier Transform Infrared Spectrometer (Nexus 870 FT-IR) to elucidate the functional groups presenting in rice straw before and after esterification. For IR spectra, 5 mg of powdered rice straw was encapsulated in 400 mg of KBr. Translucent disk was made by pressing the ground mixed materials with the aid of a bench press (955 kg for 10 min).

3. Results and discussion

3.1. Influence of initial pH

In all experimental parameters affecting basic dyes sorbed on OA-modified rice straw, the influences of initial pH were investigated first. The initial pH of dye solutions was researched over a range from 2 to 11. Because BG4 changes color and flocculates above pH 10, its sorption experiments were only conducted from pH 2 to 10. As elucidated in Fig. 1, for BB9 and BG4, the dye removal ratios were minimum at the initial pH 2. The percentages of dyes sorbed increased as the initial pH was increased from pH 2 to pH 6. Beyond pH 6, the maximum dye removal ratios were reached and the percentages of dyes

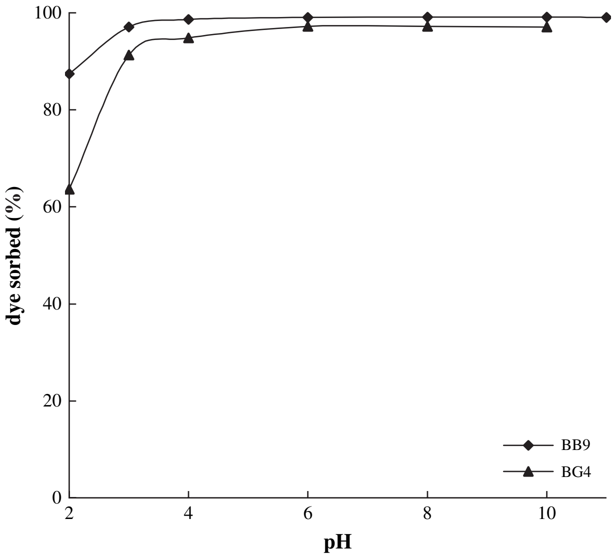

Fig. 1. Influence of initial pH on sorption of BB9 and BG4 by OA-modified rice straw (dye concentration: 250 mg/l; sorbent dose: 2 g/l; contact time: 6 h).

sorbed kept basically unchangeable. For this reason, pH 6 was selected for the other experiments.

3.2. Effect of sorbent dose

The effects of sorbent dose on the removal ratios of dyes are shown in Fig. 2. Along with the increase of sorbent dosage from 0.25 to 2.0 g/l, the percentages of dye sorbed increased from 30.41 to 99.15% and from 34.49 to 97.33% in BB9 and BG4, respectively. Above 2.0 g/l of sorbent dose, the sorption equilibria of dyes were reached and the removal ratios of dyes kept almost invariable. So, the sorbent dosage of 2.0 g/l was chosen for subsequent experiments.

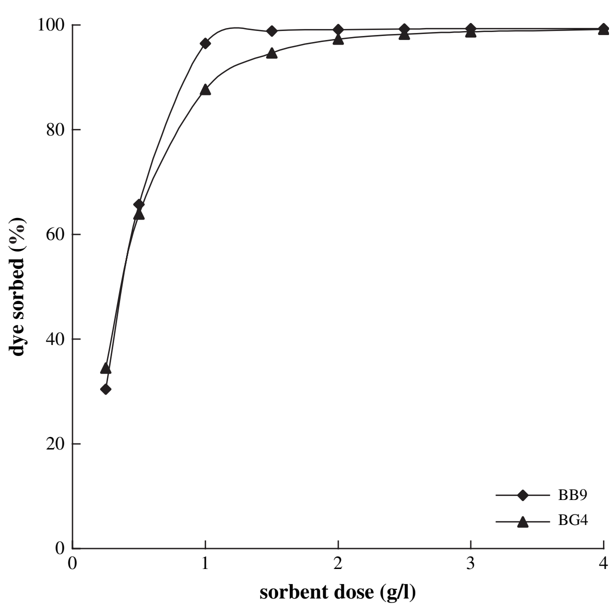

Fig. 2. Effect of sorbent dose on sorption of BB9 and BG4 by OA-modified rice straw (dye concentration: 250 mg/l; contact time: 6 h; pH: 6).

3.3. Influence of initial dye concentration

The influences of dye concentration on sorption percentages of dyes were estimated under the condition of 2.0 g/l sorbent used. As shown in Fig. 3, when the dye concentration was increased from 50 to 500 mg/l, the percentages of BB9 sorbed only decreased from 99.37 to 97.15%, but for BG4, dye sorption percentages obviously decreased from 99.34 to 89.85%.

With the data in Fig. 3, Langmuir and Freundlich equations were employed to study the sorption isotherm of BB9 and BG4.

The Langmuir equation is based on the assumption that maximum sorption corresponds to saturated monolayer of sorbate molecule on the sorbent surface, that the energy of sorption is constant and that there is no transmigration of sorbate in the plane of the surface.

The linear Langmuir equation was shown as follows:

$$C_e/q_e = 1/(aQ_m) + C_e/Q_m$$

where C_e (mg/l) is the concentration of the dye solution at equilibrium, q_e (mg/g) is the amount of dye sorbed at equilibrium, Q_m is the maximum sorption capacity and represents a practical limiting sorption capacity when the sorbent surface is fully covered with monolayer sorbate molecules and a is Langmuir constant. The Q_m and a values were obtained from the slopes ($1/Q_m$) and intercepts ($1/aQ_m$) of linear plots of C_e/q_e versus C_e.

The Freundlich equation is an empirical model and can be linearized in logarithmic form as follows:

$$\ln Q_e = \ln K + (1/n)\ln C_e$$

where Q_e is the amount of dye sorbed at equilibrium, C_e is the concentration of the dye solution at equilibrium, K and $1/n$ are empirical constants and their values were calculated from the intercepts ($\ln K$) and slopes ($1/n$) of linear plots of $\ln Q_e$ versus $\ln C_e$.

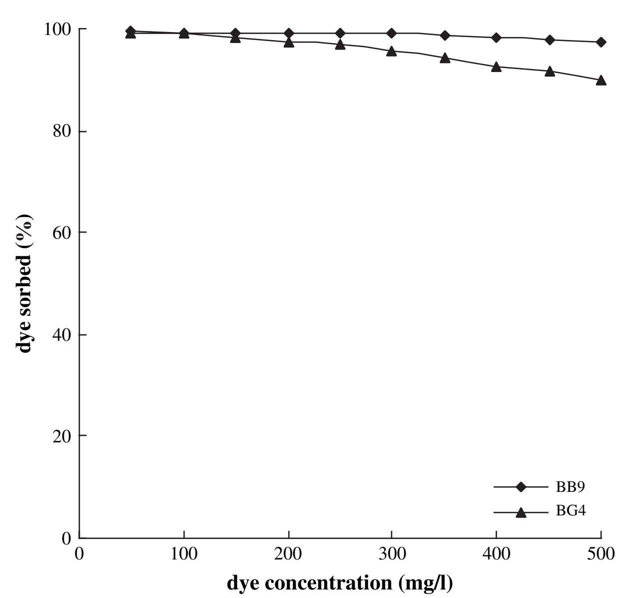

Fig. 3. Influence of dye concentration on sorption of BB9 and BG4 by OA-modified rice straw (sorbent dose: 2 g/l; contact time: 6 h; pH: 6).

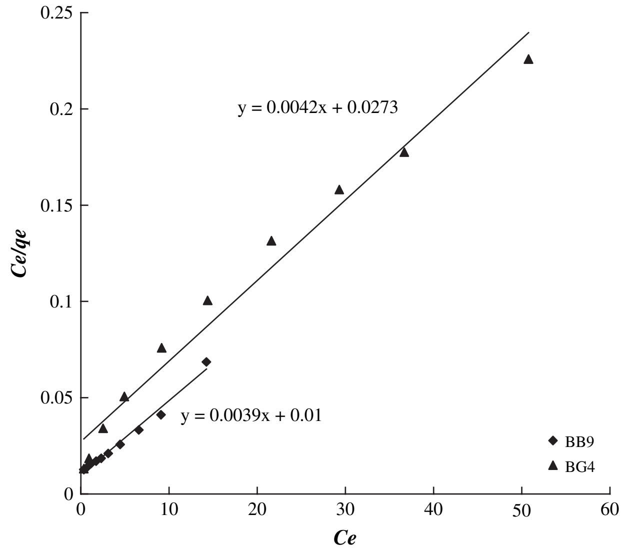

Fig. 4. The Langmuir plots for the sorption of BB9 and BG4 by OA-modified rice straw.

The Langmuir and Freundlich sorption isotherms of BB9 and BG4 sorbed on OA-modified rice straw are shown in Figs. 4 and 5. Table 1 gives the values of parameters, correlation coefficients and probability factors of the Langmuir and Freundlich equations. The experimental results indicated that the sorption isotherms of BB9 and BG4 sorbed on OA-modified rice straw followed the Langmuir and Freundlich models. The maximum sorption capacity (Q_m) of OA-modified rice straw for BB9 and BG4 was 256.4 and 238.1 mg/g, respectively.

3.4. Effect of ion strength

The effects of ion strength on BB9 and BG4 sorbed on OA-modified rice straw were tested by the addition of sodium chloride or potassium chloride to the dye solutions. The concentration of salt used ranged from 0 to 0.5 M. As seen in Fig. 6, increasing the ion strength of solution caused decrease in sorption percentages of BB9 and BG4. This could be attributed to the competition of BB9 or BG4 cations and Na^+ or K^+ ions for the sorption sites. It could also be found that the effect of K^+ ion on dye sorptions was larger than that of Na^+ ion for K^+ ion having bigger atom radius than Na^+ ion.

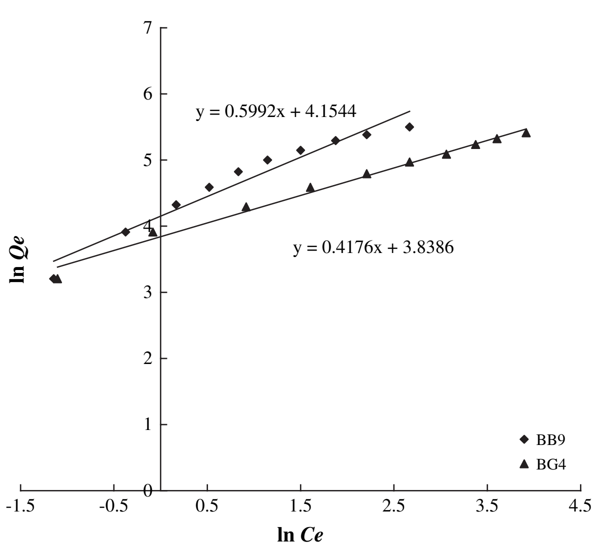

Fig. 5. The Freundlich plots for the sorption of BB9 and BG4 by OA-modified rice straw.

Table 1
The values of parameters, correlation coefficients and probability factors of Langmuir and Freundlich equations

Dye	Langmuir				Freundlich			
	Q_m (mg/g)	a	R^2	p	K	$1/n$	R^2	p
BB9	256.4	0.3900	0.9846	<0.001	63.71	0.5992	0.9543	<0.001
BG4	238.1	0.1538	0.9758	<0.001	46.46	0.4176	0.9878	<0.001

3.5. Sorption kinetics

The sorption kinetics of BB9 and BG4 sorbed on OA-modified rice straw is presented in Fig. 7. The removal rates of dyes were very rapid at the initial stages of sorption. It was caused by the fast diffusion and sorption of dye molecules onto the external surface of sorbent. After a very rapid sorption, dye uptake rates slowly declined with lapse of time and reached equilibrium values at about 2 h and 4 h for BB9 and BG4, respectively. This process was controlled by the pore diffusion velocities of dyes into the intraparticle matrix of sorbent.

The kinetic data of the first 120 min in Fig. 7 were treated with the following Ho's pseudo-second-order rate equation [29]:

$$t/q_t = 1/k_{ad}q_e^2 + t/q_e$$

where q_e and q_t (mg/g) refer to the amount of dye sorbed at equilibrium and at time t (min), respectively, and k_{ad} (g/mg min)

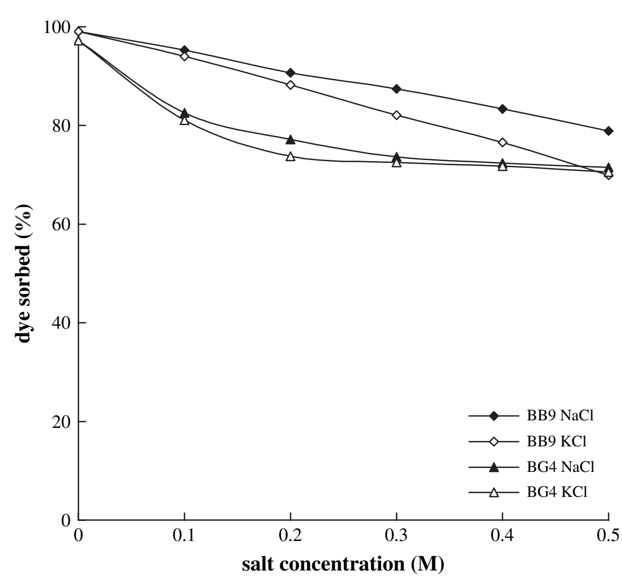

Fig. 6. Effect of ion strength on sorption of BB9 and BG4 by OA-modified rice straw (dye concentration: 250 mg/l; sorbent dose: 2 g/l; contact time: 6 h; pH: 6).

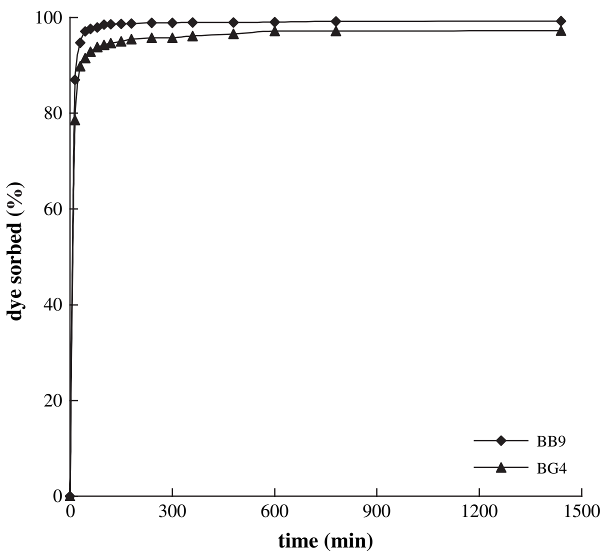

Fig. 7. Sorption kinetics of BB9 and BG4 by OA-modified rice straw (dye concentration: 250 mg/l; sorbent dose: 2 g/l; pH: 6).

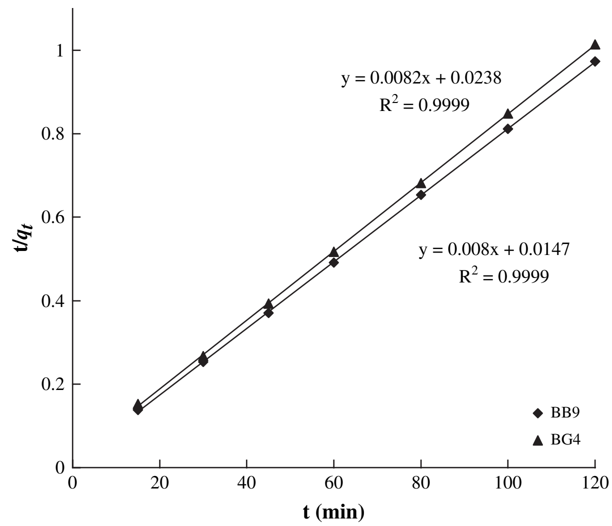

Fig. 8. The pseudo-second-order model plots of BB9 and BG4 sorbed by OA-modified rice straw.

is the rate constant. The q_e and k_{ad} values could be calculated from the slopes ($1/q_e$) and intercepts $(1/k_{ad}q_e^2)$ of linear plots of t/q_t versus t. The pseudo-second-order model plots of BB9 and BG4 sorption are shown in Fig. 8. The high values of correlation coefficients showed that the data fitted well to the pseudo-second-order rate kinetic model.

3.6. Analysis of IR spectra before and after OA esterification

The IR spectra of crude and OA-modified rice straw are shown in Fig. 9. Comparing with the IR spectrum of crude rice straw, it could been seen that there was an obvious characteristic stretching vibration absorption band of carboxyl group at 1737 cm^{-1} (indicated by arrow) in IR spectrum of OA-modified rice straw. This result confirmed the occurrence of esterifying reaction.

4. Conclusions

This study confirmed that OA-modified rice straw was an excellent sorbent for removal of basic dyes from aqueous solution. The optimal pH for favorable sorption was 6 and above. The 2.0 g/l or above of sorbent could almost completely remove BB9 and BG4 from 250 mg/l of dye solution. The ratios of BB9 and BG4 sorbed kept above 97% over a range from 50 to 250 mg/l of dye concentration when 2.0 g/l of sorbent was used. Increase in ion strength of solution induced decline of BB9 and BG4 sorption. The isothermal data fitted well to the Langmuir and Freundlich models. The sorption capacities for

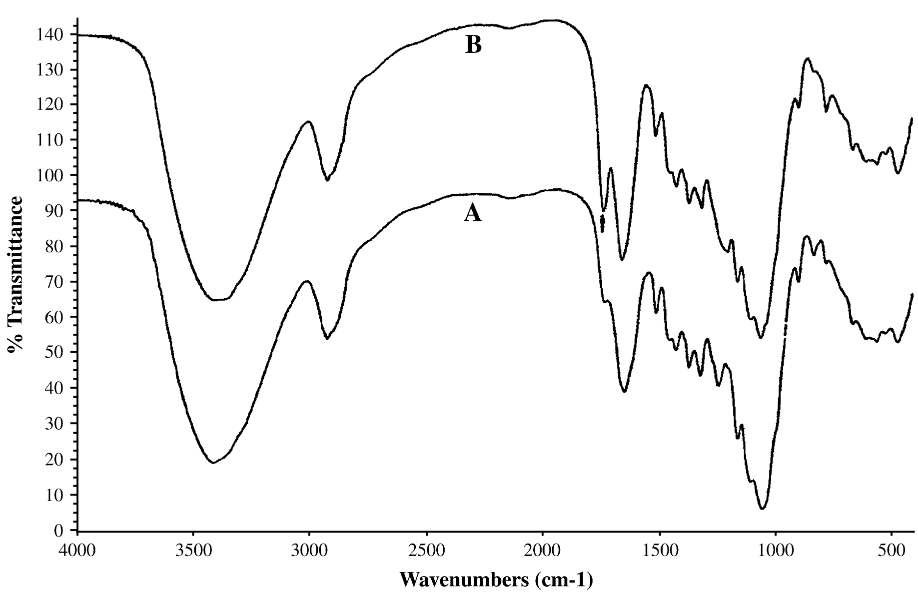

Fig. 9. IR spectra of rice straw (A: crude rice straw; B: OA-modified rice straw).

BB9 and BG4 were 256.4 and 238.1 mg/g, respectively. The sorption processes could be described by the pseudo-second-order kinetic model.

Acknowledgments

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