

Enhanced malachite green removal from aqueous solution by citric acid modified rice straw

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Abstract

In this paper, rice straw was thermochemically modified with citric acid (CA) as esterifying agent. Two introduced free carboxyl groups of esterified rice straw were further loaded with sodium ion to yield potentially biodegradable cationic sorbent. In order to investigate the effect of chemical modification on the cationic dye sorption of rice straw, the removal capacities of native and modified rice straw sorbing a cationic dye (malachite green) from aqueous solution were compared. The effects of various experimental parameters (e.g. initial pH, sorbent dose, dye concentration, contact time) were investigated. For modified rice straw (MRS), the malachite green (MG) removal percentage came up to the maximum value beyond pH 4. For the 250 mg/l of MG solution, the 1.5 g/l or up of MRS could almost completely remove the dye from aqueous solution. Under the condition of 2.0 g/l sorbent used, the percentage of MG sorbed on MRS kept above 93% over a range from 100 to 500 mg/l of MG concentration. The sorption isotherms fitted the Langmuir or Freundlich models. The sorption equilibriums were reached at about 10 h. The sorption processes followed the pseudo-first-order rate kinetics. After chemical modification, the intraparticle diffusion rate constant (k_{id}) was obviously increased. The results in this study indicated that MRS was an excellent sorbent for removal of MG from aqueous solution.

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1. Introduction

Synthetic dyes widely used in industry present certain hazards and environmental problems. Colour in waterbody is not only aesthetically unpleasant but also interferes light penetration and reduces photosynthetic action. Many dyes or their metabolites have toxic as well as carcinogenic, mutagenic and teratogenic effects on aquatic life and humans [1,2].

Activated carbon is perhaps the most widely used sorbent for removal of dyes from industrial wastewater. Although regenerative, high operating costs and problems with regeneration hamper large-scale application of activated carbon. Agricultural by-products are considered to be low value products. Because

of low utilization 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 benefit to mankind. In recent years, attention has been focused on the utilization of native [3–12] or modified [13–18] agricultural by-products as sorbent. Generally, sorption capacity of crude agricultural by-products is low. Chemical modification can greatly improve the sorption capacity of these biomaterials. Wing [19] developed a method to modify corn fiber thermochemically with citric acid. When heated, citric acid will dehydrate to yield a reactive anhydride which can react with the hydroxyl groups on the cellulose to form an ester linkage. The introduced free carboxyl groups of citric acid increase the net negative charge on the corn fiber, thereby increasing its binding potential for cationic contaminants.

Rice straw is a lignocellulosic agricultural stalk containing cellulose (37.4%), hemicellulose (44.9%), lignin (4.9%) and

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silica ash (13.1%) [20]. In China, the annual output of agricultural stalk exceeds 600 billion kg and the disposal of agricultural stalk by open-field burning frequently causes serious air pollution. Therefore, the new economical technologies for agricultural stalk disposal and utilization must be developed. In this paper, rice straw was thermochemically modified with citric acid (CA) as esterifying agent. Two introduced free carboxyl groups of esterified rice straw were further loaded with sodium ion to yield potentially biodegradable cationic sorbent. The capacities of this sorbent and native rice straw for removal of a cationic dye, malachite green (MG), from aqueous solution were compared. MG is a basic dye of triphenylmethane type (C.I.No 42,000, FW = 364.9, λ_{\max} = 617 nm). This dye is widely used for the dyeing of cotton, jute, silk, wool, leather and also extensively used all over the world in the fish farming industry as fungicide, ectoparasiticide and disinfectant. It has been shown recently that MG is linked to an increased risk of cancer. MG is highly cytotoxic to mammalian cell and also acts as a liver tumour promoter [21].

The aims of this work were: (1) to produce a new biosorbent with high cationic sorption capacity and comparatively low product cost and (2) to investigate application of this new sorbent in cationic dye wastewater treatment.

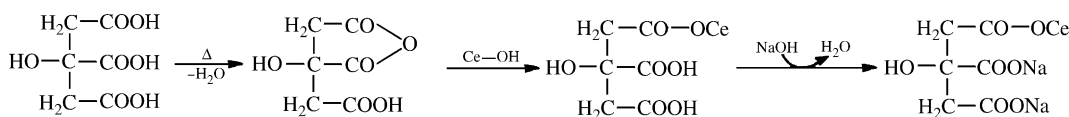
2. Materials and methods

2.1. Preparation of modified rice straw

Rice straw was collected from a local farm. After removing the rotten section, the collected biomaterial was cut into segment of 10 cm length and washed with 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 fraction for further chemical modification.

The chemical modification of rice straw was made according to the similar method previously described by Vaughan et al. [22]. Ground rice straw was mixed with 0.5 M CA 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 reaction between acid and straw was proceeded by raising the oven temperature to 120 °C for 90 min. After cooling, the CA-modified rice straw was washed with distilled water until the liquid did not turn turbidity when 0.1 M lead(II) nitrate was dropped in. After filtration, the CA-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 CA-modified rice straw was dried at 50 °C until constant weight and preserved in a desiccator as sorbent for further use.

The chemical modification of rice straw can be schematically expressed by equation:



2.2. Preparation of cationic dye solution

The cationic dye (MG), in commercial purity, was used without further purification. The MG stock solution was prepared by dissolving accurately weighted dye in distilled water to the concentration of 500 mg/l. The experimental solutions were obtained by diluting the dye stock solution 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 20 ± 2 °C using 250 ml shaking flasks containing 100 ml different concentrations and initial pH values of MG solution. The initial pH values of the solution were previously adjusted with dilute HNO₃ or NaOH using pH meter. Different doses of native rice straw (NRS) or modified rice straw (MRS) were added to each flask, and then the flasks were sealed up to prevent change of volume of the solution during the experiments. After shaking the flasks for predetermined time intervals, the samples were withdrawn from the flasks and the MG solution was separated from the sorbent by centrifugation. The pH of supernatant solution was adjusted with proper buffer solution to the natural value of dye solution according to certain proportion. MG concentration in the supernatant solution was estimated by measuring absorbance values at maximum wavelength of dye with a 752 W Grating Spectrophotometer (Shanghai, China) and computing from the calibration curve. The amount of MG sorbed on sorbent was calculated by the mass balance relationship:

$$q_e = \frac{(C_0 - C_e)V}{W}$$

The percentage of MG sorbed on sorbent was calculated by the following equation:

$$p_e (\%) = \frac{100(C_0 - C_e)}{C_0}$$

where q_e and p_e are the amount (mg/g) and percentage (%) of MG sorbed at equilibrium, C_0 and C_e the initial and equilibrium liquid-phase concentration of MG, respectively (mg/l), V the volume of the solution (l) and W is the weight of the sorbent (g).

The effect of each experimental parameter was studied by fixing the values of other parameters. The experiments were conducted in duplicate and the negative controls (with no sorbent) were simultaneously carried out to ensure that sorption was by sorbents and not by the container.

2.4. IR spectra study

The IR spectra of NRS and MRS were performed on a Fourier transform infrared spectrometer (Nexus 870 FT-IR) to elucidate

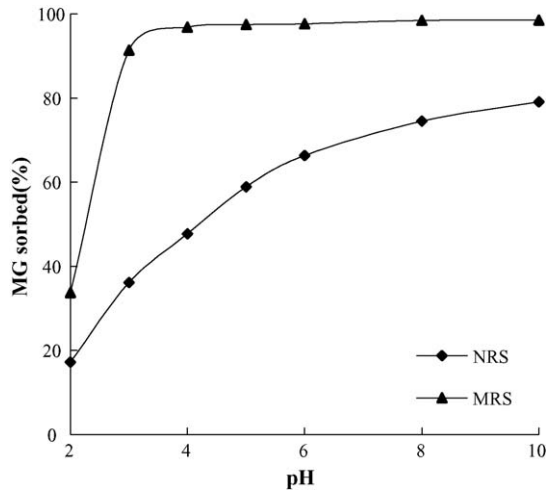


Fig. 1. Influence of initial pH on sorption of MG by NRS and MRS (MG concentration: 250 mg/l; sorbent dose: 2 g/l; contact time: 10 h).

the functional groups presenting in rice straw before and after esterification. For IR spectra, 5 mg of sorbents was encapsulated in 400 mg of KBr. Translucent disk was made by pressing the ground mixed material 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 MG sorbed on NRS and MRS, the influences of initial pH were studied first. The initial pH of dye solution was researched over a range from 2 to 10. As elucidated in Fig. 1, for NRS and MRS, the dye removal percentages were minimum at the initial pH 2. For NRS, its main functional group is hydroxyl group. Along with increase of pH value, the concentration of H^+ ions that compete with the dye cation for the sorption sites decreased, the percentage of MG sorbed on NRS gradually increased as the initial pH was increased from pH 2 to pH 10. For MRS, its practical functional group is carboxyl group and the pK value of carboxyl group is $3 \pm$. When $pH < 3$, the non-ionic form of carboxyl group, $-COOH$, was presented, MG sorption was small because of the absence of electrostatic interaction. When $pH > 3$, carboxyl group is turned into $-COO^-$, MG sorption is increased, but the MG removal percentage was not significantly altered beyond pH 4. For above reasons, the pH 6 was selected for the other experiments.

3.2. Effect of sorbent dose

The effects of sorbent dose on the removal percentages of MG are shown Fig. 2. Along with the sorbent dose was increased from 0.5 to 5.0 g/l, the percentages of MG sorbed on NRS increased from 28.57 to 80.17%. When the sorbent dose was increased from 0.5 to 2.0 g/l, the percentages of MS sorbed on MRS increased from 62.29 to 97.68%. Increase in the sorption percentage of MG with sorbent dose could be attributed to

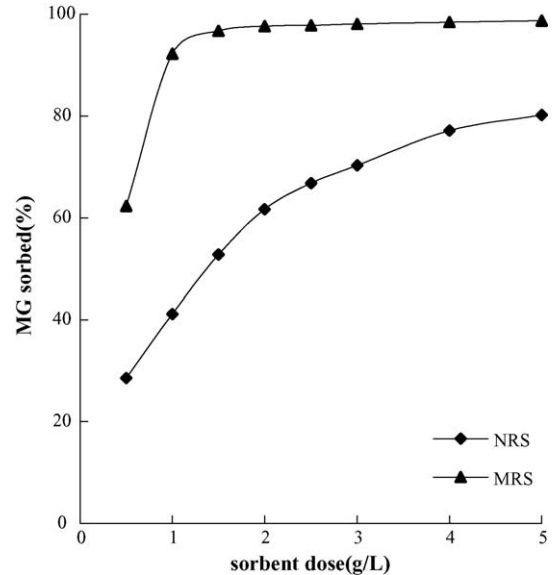


Fig. 2. Effect of sorbent dose on sorption of MG by NRS and MRS (MG concentration: 250 mg/l; contact time: 10 h; pH 6.0).

increased sorbent surface area and availability of more sorption sites. Above 2.0 g/l of sorbent dose, the maximum uptake value of MG sorbed on MRS was reached and the removal percentage of MG only oscillated between 97.68 and 98.73%.

3.3. Influence of initial dye concentration

The influences of dye concentration on sorption percentages of MG were estimated. As shown in Fig. 3, when the dye concentration was increased from 100 to 500 mg/l, the percentage of MG sorbed on NRS sharply decreased from 87.73 to 34.27%, but the percentage of MG sorbed on MRS decreased a little, only from 99.2 to 93.1%.

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

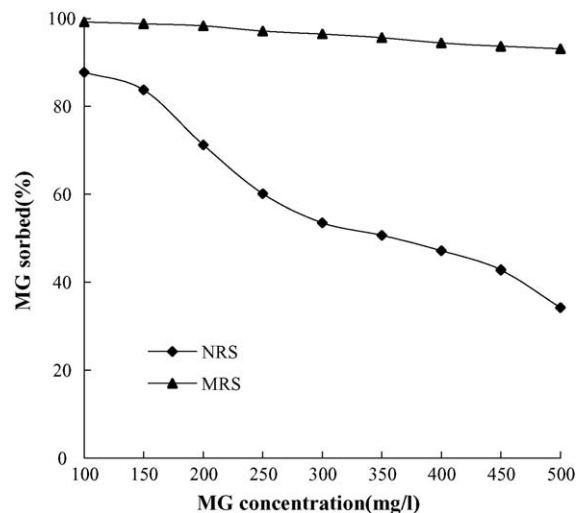


Fig. 3. Influence of dye concentration on sorption of MG by NRS and MRS (sorbent dose: 2 g/l; contact time: 10 h; pH 6.0).

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:

$$\frac{C_e}{q_e} = \frac{1}{aQ_m} + \frac{C_e}{Q_m}$$

where C_e (mg/l) is the concentration of the dye solution at equilibrium, q_e (mg/g) the amount of dye sorbed at equilibrium, Q_m 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:

$$\ln Q_e = \ln K + \left(\frac{1}{n}\right) \ln C_e$$

where Q_e is the amount of dye sorbed at equilibrium, C_e 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 $\ln C_e$.

The Langmuir and Freundlich sorption isotherms of MG sorbed on NRS and MRS are shown in Figs. 4 and 5. Table 1 gives the values of parameters and correlation coefficients of the Langmuir and Freundlich equations. The experimental results indicated that the sorption isotherms of MG sorbed on MRS followed the Langmuir and Freundlich models, but the sorption isotherms of MG sorbed on NRS only fitted the Langmuir model. The maximum sorption capacity (Q_m) of NRS and MRS for MG was 94.34 and 256.41 mg/g, respectively.

3.4. Sorption kinetics

The mechanism for the sorption of MG on sorbent may be assumed to involve the following sequential steps [23]:

- Migration of MG from bulk of the solution to the boundary layer of the sorbent.
- Diffusion of MG through the boundary layer to the surface of the sorbent.
- Intraparticle diffusion of MG into the interior pores of the sorbent particle.

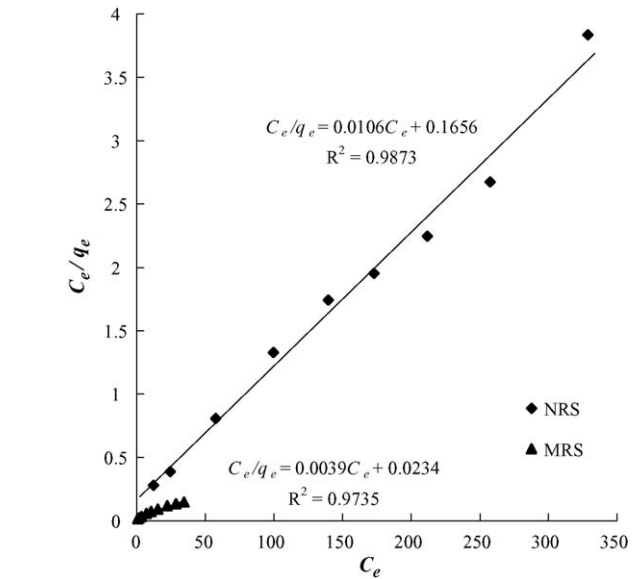


Fig. 4. The Langmuir plots for the sorption of MG on NRS and MRS.

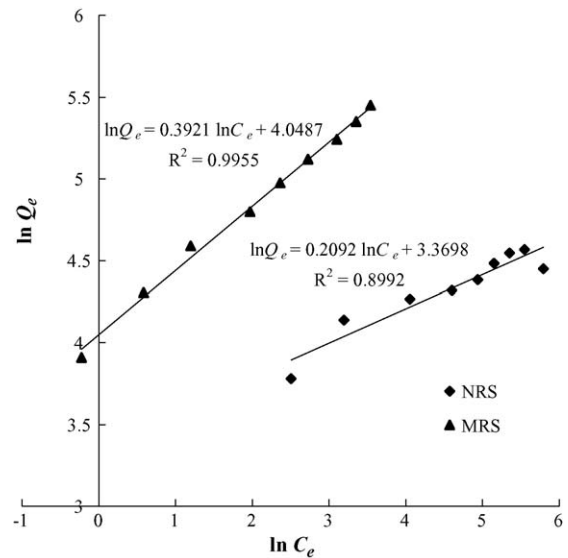


Fig. 5. The Freundlich plots for the sorption of MG on NRS and MRS.

- Sorption of MG at an active site on the exterior or interior surface of sorbent.

Fig. 6 illustrates the sorption kinetics of MG sorbed on NRS and MRS. The removal rates of MG were very rapid during the initial stages of the sorption processes. After a very rapid sorp-

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

Sorbent	Langmuir			Freundlich		
	Q_m (mg/g)	a	R^2	K	$1/n$	R^2
NRS	94.34	0.064	0.9873	29.07	0.2092	0.8992 ^a
MRS	256.41	0.167	0.9735	57.32	0.3921	0.9955

^a $R^2 = 0.8992 \ll 1$, the Freundlich model was not fitted.

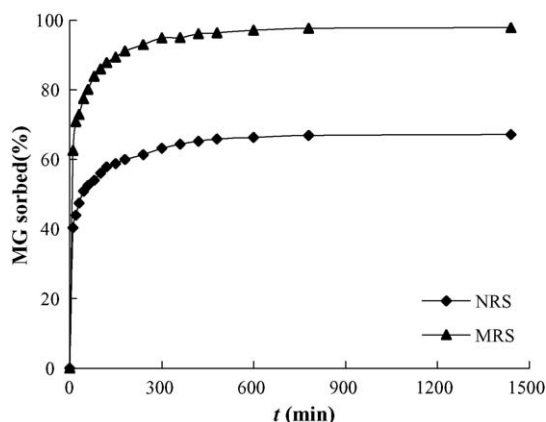


Fig. 6. Sorption kinetics of MG by NRS and MRS (MG concentration: 250 mg/l; sorbent dose: 2 g/l; pH 6.0).

tion, MG uptake rates slowly declined with lapse of time and reached equilibrium values at about 10 h for NRS and MRS. The three phases of MG sorptions could be attributed to boundary layer diffusion sorption, intraparticle diffusion sorption and sorption equilibrium, respectively.

The kinetic data of the first 2 h in Fig. 6 are handled with the following Lagergren’s pseudo-first-order rate equation:

$$\log(q_e - q_t) = \frac{\log q_e - k_{ad}t}{2.303}$$

where q_e and q_t (mg/g) refer to the amount of dye sorbed at equilibrium and time t (min), respectively, and k_{ad} is the rate constant. The rate constants k_{ad} could be calculated from the slopes of the linear plots of $\log(q_e - q_t)$ versus t . The Lagergren plots of MG sorption are shown in Fig. 7. The high values of correlation coefficients showed that the data conformed well to the pseudo-first-order rate kinetic model.

The intraparticle diffusion rate constants (k_{id}) were also researched by treating the kinetic data of the first 120 min in

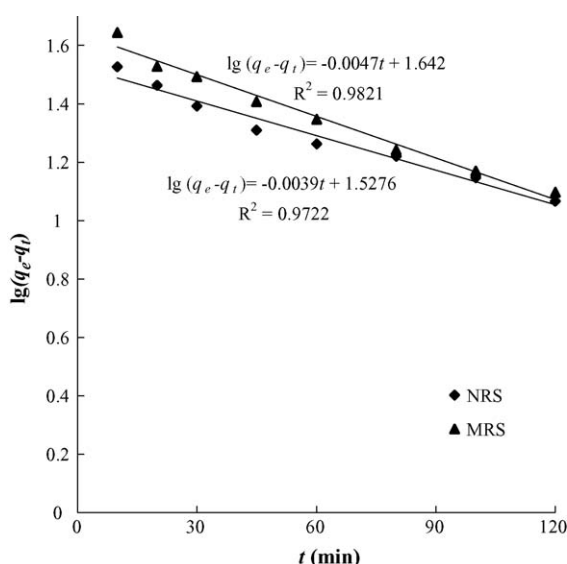


Fig. 7. Lagergren plots for sorption of MG by NRS and MRS.

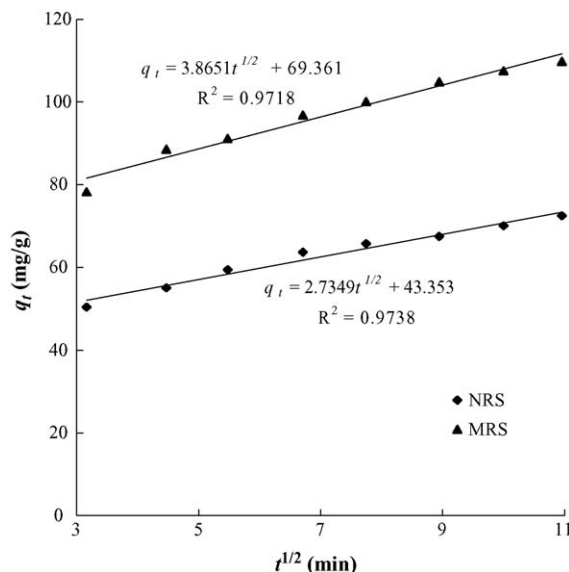


Fig. 8. Plots of q_t vs. $t^{1/2}$ for intraparticle transport of MG sorbed on NRS and MRS.

Fig. 6 with the following intraparticle diffusion rate equation:

$$q_t = k_{id}t^{1/2}$$

where q_t is the amount of dye sorbed (mg/g) at time t (min). k_{id} values were obtained from the slopes of the linear plots of q_t versus $t^{1/2}$. The intraparticle diffusion rate plots of MG sorbed on NRS and MRS are shown in Fig. 8. The k_{id} value was increased from 2.73 to 3.87 mg/g min^{1/2} due to citric acid modification.

3.5. Analysis of IR spectra before and after citric acid esterification

The IR spectra of NRS and MRS are shown in Fig. 9. Comparing with the IR spectrum of NRS, it could be seen that there was a strong characteristic stretching vibration absorption band of carboxyl group at 1737 cm⁻¹ in IR spectrum of MRS. It reflected the result of citric acid esterification.

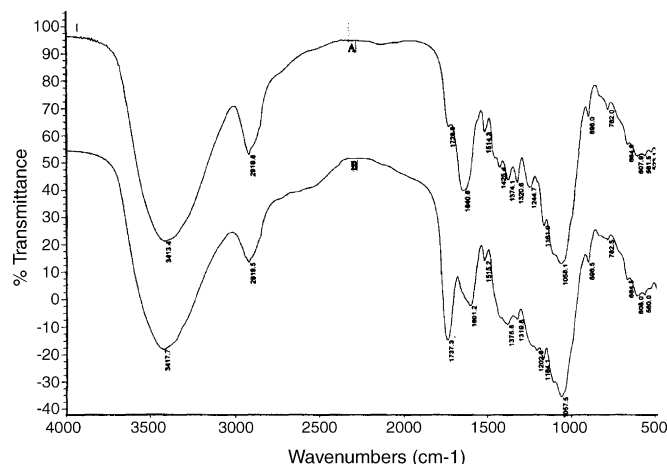


Fig. 9. IR spectra of NRS and MRS. (A) NRS and (B) MRS.

4. Conclusions

This study showed that MRS was an excellent sorbent for removal of cationic dye, MG, from aqueous solution. The initial pH of dye solution did not significantly affect sorption of MG on MRS over a wide pH range, the optimal pH for favorable sorption of MG on MRS was 4 and above. But the initial pH of dye solution did have some effect on the MG sorption on NRS. The trend that the percentage of MG sorbed increased as the sorbent dose was increased could be seen. For the 250 mg/l of MG solution, the 1.5 g/l or up of MRS could almost completely remove the dye from aqueous solution. Under the condition of 2.0 g/l sorbent used, the percentage of MG sorbed on MRS kept above 93% over a range from 100 to 500 mg/l of MG concentration, yet the percentage of MG sorbed on NRS decreased as the MG concentration was increased. The sorption isotherms of MG sorbed on MRS followed the Langmuir and Freundlich models, but the sorption isotherms of MG sorbed on NRS only fitted the Langmuir model. The sorption capacities were found to be 94.34 and 256.41 mg MG per gram of NRS and MRS, respectively. The sorption equilibriums were reached at about 10 h. The sorption processes followed the pseudo-first-order rate kinetics. After citric acid modification, the intraparticle diffusion rate constant (k_{id}) was obviously increased.

Acknowledgments

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