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Adsorptive removal of Cd(II) from aqueous solution using natural and modified rice husk

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ABSTRACT

In this study, the natural and modified rice husk were tested to remove Cd(II) ions from water. The modified rice husk was prepared by being treated with alkali. The results showed the Cd(II) adsorption capacity was 73.96, 125.94 mg/g, respectively, for the natural and modified rice husk. The modified rice husk had faster kinetics and higher adsorption capacities than the natural rice husk, which can be attributed to the surface structural changes of the material. Equilibrium adsorption data are more consistent with the Langmuir isotherm equation than with the Freundlich equation. The Cd(II) adsorption on the two adsorbents tends to increase with the increase of pH. The optimum pH for Cd(II) adsorption is 6.5. Both pseudo-first-order and pseudo-second-order equations were able to describe properly the kinetics of Cd(II) adsorption. The desorbability of Cd(II) is about 95.8–99.1% by 0.1 M HCl solution.

1. Introduction

In case of cadmium is a highly toxic element affecting the environment and considered to be carcinogenic, the discharged in effluent will be absorbed and accumulated by microorganisms. Eventually, cadmium will be transferred to humans via the food chain, and cause serious damage to kidney and bones (Leyva et al., 1997). Typical Cd(II) removal methods such as chemical precipitation (Pengthamkeerati et al., 2008), reverse osmosis (Mohsen-Nia et al., 2007), ion exchange (Pehlivan and Altun, 2007), and electrochemical treatment (Singh et al., 1998) have been successfully applied. However, increasing attention has been paid to adsorptive removal of cadmium from aqueous solutions. The application of low-cost and easily available materials in wastewater treatment has been widely investigated during recent years, such as clarified sludge (Naiya et al., 2008), activated alumina (Naiya et al., 2009a), rice husk ash (Srivastava et al., 2006, 2009; Naiya et al., 2009b), sawdust (Taty et al., 2003; Naiya et al., 2009c), neem bark (Naiya et al., 2009c) and wheat bran (Singh et al., 2006).

Rice husk is agricultural waste, accounting for about one fifth of the annual gross rice, 545 million metric tons, of the world. Rice husk contains abundant floristic fiber, protein and some functional groups such as carboxyl, hydroxyl and amidogen (Nakbanpote et al., 2007), which make the adsorption processes possible. And it has been successfully used to remove colored component (Vadivelan and Kumar, 2005; Han et al., 2008), metal ions (Srivastava et al., 2006, 2009; Naiya et al., 2009b) from water. Its adsorption capacity can be increased by modifying its texture by means of chemical and/or thermal treatments (Hsu and Pan, 2007). But there are fewer reports about the removal of cadmium from water using modified rice husk. Therefore, adsorption studies of Cd(II) on natural and modified rice husk were carried out in detail.

2. Methods

2.1. Materials

The natural rice husk (NRH) used in the present experiments was obtained from a market at Jingshan County, Hubei Province, China. Its chemical compositions are presented in Table 1. The sample used was ground and screened. And the particles between 75 μm and 90 μm were selected. The modified rice husk (MRH) sample was prepared by alkali treatment. Alkali treatment was carried out by placing the NRH sample in contact with NaOH (1 M), with constant stirring for 24 h. The liquid/solid ratio was 10 mL/g. The slurry was allowed to settle for 48 h. It was then filtered, washed OH^- free with distilled water, and dried at 105 °C for 6 h to constant weight. And it was ground and screened. Then the MRH particles between 75 μm and 90 μm were selected and preserved at room temperature in a sealed bottle.

The Cd(II) stock solution containing 1000 mg Cd/L was prepared by dissolving cadmium nitrate ($Cd(NO_3)_2$) powders (analytical reagent grade) in distilled water. Cd(II) working solutions in different

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Table 1
Chemical composition of the NRH.

Chemical composition	(%)
Cellulose	32.35
Hemicellulose	21.62
Lignin	21.55
Mineral compositions	15.14
Water	8.06
Others	1.28

concentrations were prepared by diluting the Cd(II) stock solution with distilled water. The pH value of the Cd(II) working solution was adjusted to 6.5–6.8 with diluted HCl and NaOH before adsorption experiments.

2.2. FT-IR analysis

The surface structure of the materials was investigated with FT-IR. The IR spectra of each sample were recorded on a Perkin–Elmer 1725X spectrophotometer to check the change in the functional group of the sample surface after alkali treatment, specimens being examined in the form of KBr disks.

2.3. Study of adsorption isotherms

Cd(II) adsorption isotherms study was carried out with different initial concentrations of Cd(II) and a fixed concentration of the adsorbents at room temperature (25 °C). One hundred milligrams of the sample was loaded in a 250-mL Erlenmeyer flask, and 100 mL of Cd(II) solution was then added. Nine levels of initial Cd(II) concentrations (20, 30, 50, 80, 100, 200, 400, 600, 800 mg/L) were used. The pH of the solution was maintained at a defined value (6.5–6.8) by manually adding 0.1 M HCl or 0.1 M NaOH solutions at intervals of every 45–60 min. The flask was capped and stirred magnetically at 120 rpm for 24 h to ensure approximate equilibrium. At the end of the adsorption period, the solution was filtered through a 0.45 μm membrane filter and then analyzed for Cd(II). The quantity of adsorbed Cd(II) (adsorption capacity) was calculated from the decrease of the Cd(II) concentration in solution. The isotherm data on Cd(II) adsorption were fitted to Langmuir and Freundlich equations. The duplicate experiments demonstrated the high repeatability of this adsorption method and the experimental error could be controlled within 5–10%.

2.4. Effect of pH on Cd(II) adsorption

With a similar procedure, the effect of pH on Cd(II) adsorption was examined in a series of experiments that used the same initial Cd(II) concentration (20 mg/L) while maintaining pH at different values between 1.5 and 8.5.

2.5. Adsorption kinetic measurements

Cd(II) adsorption kinetics was evaluated at room temperature (25 °C) and an initial Cd(II) concentration of 20 mg/L (corresponding to initial loading 20 mg Cd(II)/g adsorbent). Before the start of each kinetic experiment, 500 mg of the sample was loaded in a 1-L Erlenmeyer flask. Then 500 mL of Cd(II) solution (20 mg/L) was added into the flask. The flask was covered with magnetic stirring at 120 rpm. The pH of the solution was maintained at a defined value (6.5–6.8). And it was adjusted with 0.1 M HCl or 0.1 M NaOH solutions by using a pH meter. Several mL of reaction solution was sampled intervals between 0 and 24 h of adsorption. The sampled solution was immediately filtered through a 0.45 μm membrane filter and then analyzed for Cd(II).

2.6. Desorption studies

To evaluate Cd(II) desorption from the samples, the residual solids retained on the filter paper were collected in a 250-mL Erlenmeyer flask after filtration of the suspension from an adsorption test. To each flask 100 mL of 0.1 M HCl solution was added. The flask was covered with magnetic stirring at 120 rpm for 24 h while pH was maintained at the same value as in the desorption experiment. The suspension solution was filtered and analyzed for Cd(II) in a similar way described previously. The quantity of desorbed Cd(II) was determined by the amount of Cd(II) in solution after the desorption experiment.

2.7. Analysis of Cd(II)

The analysis of Cd(II) was done spectrophotometrically using atomic absorption spectrophotometer (VARIAN SPECTRA AA55, USA) as procedure laid down in APHA (1998). Each analysis point was an average of three independent parallel sample solutions. Triplicate tests showed that the standard deviation of the results was ±5%.

3. Results and discussion

3.1. Infrared spectra

The chemical structure of the adsorbent is of vital importance in understanding the adsorption process. The FT-IR technique is an important tool to identify the characteristic functional groups, which are instrumental in adsorption of metal ions. The FT-IR spectra of NRH and MRH are shown in Fig. 1. The FT-IR spectra of NRH is similar to that of previous studies (Srivastava et al., 2006, 2009; Nakbanpote et al., 2007). The broad band and peaks show that the NRH sample contained functional groups of the standard polymers α-cellulose, coirpith-lignin. And the characteristics indicate that –CO–, –OH, –C–OH, –Si–H, Si–O–Si and –Si–OH are effective in the adsorption Cd(II) onto NRH. As shown in Fig. 1, after the NRH was modified with alkali, the FT-IR spectra of MRH showed that some peaks (856 cm^{-1}, 1350 cm^{-1}, and 1381 cm^{-1}) disappeared and the broad band (2900–3700 cm^{-1}) weakened, which indicated that the surface structure of the NRH was changed.

The FT-IR spectra of Cd(II) loaded NRH and MRH are also illustrated in Fig. 1. The FT-IR spectra for Cd(II)-loaded NRH shows the disappearance of bond around 3008 cm^{-1}, and shifting of bands about 2368 cm^{-1} to lower wave number. The disappearance of bands is also observed in the Cd(II)-loaded MRH spectra around 1303 cm^{-1}, and shifting of bands about 1080 cm^{-1} to higher wave number. This means that the functional groups at these wave numbers participate in the Cd(II) adsorption.

3.2. Cd(II) adsorption isotherm

The results of the Cd(II) adsorption isotherm experiments are shown in Fig. 2. The Cd(II) adsorption capacity increased with the Cd(II) equilibrium concentration increasing from 5 to 750 mg/L. This capacity of the NRH and MRH was approximately 62.58, 118.84 mg/g, respectively, at the Cd(II) equilibrium concentration of 300 mg/L and pH 6.5–6.8. With a further increase of the Cd(II) equilibrium concentration, the increase of the adsorption capacity was less significant.

According to the results of the Cd(II) adsorption isotherm experiments, the MRH had higher adsorption capacities than the NRH. It was believed that the surface structural changes of the material play the most important role in the adsorption capacities of the Cd(II). When the NRH sample was treated with 1 M NaOH, the sur-