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ORIGINAL PAPER

Adsorption of anionic dye on magnesium hydroxide-coated pyrolytic bio-char and reuse by microwave irradiation

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Abstract Magnesium hydroxide-coated pyrolytic bio-char composite was prepared by chemical precipitation, and the adsorption behavior of anionic dye (directly frozen yellow) onto magnesium hydroxide-coated pyrolytic bio-char was investigated in the batch mode. The Fourier transform infrared spectroscopy, X-ray diffraction spectroscopy and X-ray fluorescence spectroscopy of adsorbents were characterized. Adsorption studies were performed at different pH, salt concentration, contacting time and dye concentration. The pH value of the solution influenced the adsorption capacity significantly, and adsorption is favored of pH 6–8. Salt coexisted in solution increased slightly directly frozen yellow adsorption capacity. The isotherm data were analyzed by Langmuir and Freundlich isotherm model, and Langmuir model was better to predict the equilibrium data. Thermodynamic calculations showed that the adsorption was a spontaneous and endothermic process. Exhausted magnesium hydroxide-coated pyrolytic bio-char was treated by microwave irradiation, and yield of regeneration was 98 % in the case of microwave irradiated time 5 min at 320 W. The magnesium hydroxide-coated pyrolytic bio-char can be reused.

Keywords Adsorption isotherm · Characterization · Directly frozen yellow · Regeneration · Thermodynamic parameters

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Introduction

Synthetic dyes are widely used in many industries such as textile, leather, paper, printing, paint, pigments, cosmetics, rubber, plastic, pesticide and pharmaceutical industry. Approximately 12 % of synthetic dyes are lost during manufacturing and processing performances, and 20 % of these lost dyes will enter the industrial wastewaters (Gupta and Suhas 2009). The effluent discharged into natural water bodies can pose hazardous effects on the living systems because of carcinogenic, mutagenic, allergenic and toxic nature of dyes (Robinson et al. 2001), which result in micro-toxicity to fish and other organisms. The methods for removal of dyes from solution are chemical precipitation, membrane filtration, electrodialysis, ultrafiltration, oxidative degradation, ion exchange, adsorption and biological treatment (Robinson et al. 2001). Among these methods, adsorption is a well-known and good technique for removal of refractory pollutants (including synthesis dyes) because of its easy operation, insensitivity to toxic or harmful substances, ability to treat concentrated solution of pollutant and the possibility of reusing the exhausted adsorbent through regeneration. Many low-cost adsorbents have been used for pollutant removal, and some reviews have been published (Gupta and Suhas 2009; Wang and Peng 2010; Wan Ngah and Hanafiah 2008). So, some raw or natural agricultural by-product and carbonaceous materials as low-cost adsorbents have been tested to evaluate their efficiency in the removal of dyes and other pollutants (Bhatnagar and Sillanpaa 2010; Han et al. 2009a; Wu et al. 2009). However, some raw agricultural by-products have many disadvantages, and one of them is the leaching of some organic pollutants, which may result in further pollution. This problem could be simply avoided by carbonization of the raw materials or chemical modification. Activated carbons, prepared from agricultural materials, had good adsorption capacities with respect to heavy metals, humic acid, phenol and dyes (Ioannidou and Zabaniotou 2007). The promising results were obtained when carbonaceous material prepared was utilized as adsorbent for wastewater treatment.

Bio-oil production from biomass pyrolysis may lead to the formation of solid residue, bio-char. Bio-char is different from that formed by partial combustion. In the field of biomass thermal conversion, attention is focused on the liquid or gas product (bio-oil or bio-gas), and the bio-char, which is an attractive by-product, has received attention in recent years (Arami-Niya et al. 2012; Qiu et al. 2009). It is available for this carbonaceous residue used as soil amendment except direct combustion for heat production (Lee et al. 2010). The bio-char from pyrolytic process has been directly used as adsorbents for removal of heavy metals (Mohan et al. 2011), and there are some papers about removal of dyes from solution. As biomass pyrolysis to liquid and gas fuels is important in future, it can be estimated that large amounts of these chars will be available (Bridgwater 2012). Thus, this crude bio-char is easily obtained at low cost. Any use in excess of its value will be promising, especially development in environmental field as effective adsorbent, carrier materials. Pyrolytic bio-char (PC) from wheat straw has been directly used as adsorbent to remove neutral red and methylene blue from solution, and there is some ability to bind cationic dyes (Liu et al. 2012; Zhang et al. 2011). But binding capacity of the bio-char for anionic dyes is very low.

In order to improve adsorbent's ability for removal of refractory pollutants, metal oxides-coated materials have been studied because of their potential application as effective adsorbents. Iron and manganese oxide is widely used to coat zeolite, bentonite, sand or other materials (Eren et al. 2009; Han et al. 2009b; Zhao et al. 2010; Zhu et al. 2012; Zou et al. 2006, 2009) for removal of metals or dyes, but magnesium compounds are seldom used. E. Eren et al. prepared magnesium oxide-coated bentonite for removal process of copper ions from aqueous solution (Eren et al. 2010). Ding et al. prepared magnesium salt–modified sand for removal of cadmium ions from solution (Ding et al. 2011). Sun et al. prepared magnesium hydroxide/activated carbon composite and investigated adsorption property in the weak acid red. The results showed that the composite improved the anionic dyes removal efficiency compared to activated carbon (Sun et al. 2011).

Organic refractory pollutants are difficult to degrade, and it will cause the secondary pollution if the exhausted adsorbent is placed in open air. The request for regeneration of adsorbents which is affordable and environmental friendly is inevitable. Compared to conventional thermal regeneration, application of microwave energy has the capability of molecular-level heating, which leads to homogeneous and quick thermal reactions (Jones et al. 2002). The microwave irradiation technology was successfully used to prepare and regenerate activated carbons (Liu et al. 2004; Yuen and Hameed 2009). But not much research has been carried out on regeneration of the dye-loaded adsorbents by microwave irradiation (Han et al. 2010).

Wheat straw obtained from agriculture as byproduct is vast. Thus, it is of low cost and can be easily obtained in all over the north of China. So wheat straw can be used as original materials to produce bio-oil or bio-gas through pyrolytic process and bio-char can be obtained. The objective of this study was to prepare magnesium hydroxide-coated pyrolytic bio-char (MC), to investigate characteristics of MC and to test the properties as an adsorbent for removal of anionic dye, directly frozen yellow (DFY), from synthetic solutions in batch system. Fourier transform infrared spectroscopy (FTIR), X-ray diffraction spectroscopy (XRD) and X-ray fluorescence spectroscopy (XFS) were employed to characterize PC and MC. The system variables studied included pH, salt concentration strength, contact time and DFY concentration. Equilibrium isotherm data were fitted to Langmuir and Freundlich equations, and the process was spontaneous and endothermic from thermodynamic parameters. The exhausted MC can be reused through regeneration by microwave irradiation. The experiments were conducted from October 8, 2011, to December 31, 2011, at physical–chemical building in Zhengzhou University.

Materials and methods

Materials

Pretreatment of pyrolytic bio-char (PC)

Wheat straw pyrolytic char was obtained from Research Institute of Environmental Sciences, Zhengzhou University. It was produced by slow pyrolysis of wheat straw (from local countryside) in a fluidized reactor. Wheat straw was air-dried for 1 day and was ground and sieved to a particle size of 2 mm before use. The pyrolytic temperature was up to 550 °C, and the time through the fluidized bed to produce bio-oil and bio-gas was 5 min. Yield of bio-char was about 30 % of wheat straw. PC as a by-product was washed with distilling water and dried at 110 °C in oven. Next PC was ground and sieved, and 20–40 mesh was selected for next use.

Preparation of magnesium hydroxide-coated pyrolytic char (MC)

Magnesium chloride and sodium hydroxide were mainly used in the coating of PC to enhance the adsorption capacity of PC for anionic dyes removal. Five grams of PC was immersed in 20 mL magnesium chloride solution (5 mmol Mg/g PC). Then, sodium hydroxide solution of 2 mol/L (molar ratio OH/Mg 1.5) was slowly poured into the mixture with moderate stirring and kept for 24 h. Next, the medium was filtered, and the mixture was placed in muffle furnace and heated at 300 °C for 2 h. After cooling, MC was obtained and washed and adjusted to pH 7.0 using distilled water. Finally, MC was dried at 110 °C and stored in glass bottle for further use.

Characterization of MC

Contents of carbon, hydrogen and nitrogen in PC and MC were determined by elemental analysis instrument (Flash EA 1112, USA). Elemental compositions were obtained by X-ray fluorescence spectrometer (Philips PW 2404 X-ray fluorescence, Netherlands).

The functional groups present in PC and MC were characterized by a Fourier transform infrared spectrometer (PE-1710, USA). Ten milligram of dried PC and MC was dispersed in 200 mg of spectroscopic-grade KBr to record the spectra using potassium bromide disks to prepare the bio-char samples. The spectral range varied from 4,000 to 400 cm^{-1}.

X-ray diffraction (XRD) analysis was carried out to identify any crystallographic structure using a computer-controlled X-ray diffractometer.

The pH at point zero charge (pH_{pzc}), namely the pH value required to give zero net surface charge in solution, was evaluated by the solid addition method, and it was 7.8 and 8.6 for PC and MC, respectively (figure was not shown). The specific surface area of MC and PC was tested using the nitrogen adsorption method, and the results were 22.52 and 23.76 m^2/g for PC and MC, respectively. Area of PC was slightly increased after modification. The average pore diameters of PC and MC were 19.18 and 18.87 nm, respectively.

Chemicals

All reagents used were of analytical purity. DFY (CAS 2870-32-8, $C_{30}H_{26}N_4Na_2O_8S_2$, C.I. 24895, FW = 680.66) was purchased from Zhengzhou Chemical Company, China. DFY was existed as anionic ions in water solution. Stock solution was prepared by dissolving 1.0 g of DFY in 1 L distilled water without further purification. The test solutions were prepared by diluting stock solution to the desired concentration. The pH was adjusted using 1 mol/L NaOH or HCl solutions if necessary.

Adsorption experiments

In this study, 20 mL of dye solution of initial dye concentration of 50 mg/L was agitated with 0.010 g MC in 50-mL capped conical flasks for 10 h, which was sufficient to reach equilibrium for effects of pH and ionic strength at 303 K. The contact was made using a water bath shaker at a constant temperature and at a constant agitation speed of 100 rpm.

Kinetic experiments were carried out as follows: 0.010 g of MC and PC was loaded into conical flasks containing 20 mL of dye solution (50 g/L). The flasks were then subjected to agitation using water bath shakers for various contact time intervals at 303 K. Flasks were taken from the shakers at regular time intervals.

In order to study adsorption equilibrium, 20 mL dye solution with various initial dye concentrations (NaCl solution 0.004 mol/L) was agitated with 0.010 g MC in 50-mL capped conical flasks for 10 h at 293, 303, 313 K, respectively.

After adsorption, the mixtures were centrifuged, and the left out concentration in the supernatant solution was analyzed using a UV/Vis-3000 spectrophotometer (Shimadzu Brand UV-3000) by monitoring the absorbance changes at a wavelength of maximum absorbance (400 nm). Calibration curves were plotted between absorbance and concentration of the dye solution.

Adsorbed DFY was calculated from the difference between DFY initially added to the system and that remaining in the solution after adsorption. The amount of dye adsorbed onto unit weight of adsorbent (q) was calculated using the following equation:

$$q = \frac{V(c_0 - c_e)}{m} \tag{1}$$

where V is the solution volume in L, c_0 is the initial DFY concentration in mg/L, c_e is the DFY concentration at adsorption equilibrium in mg/L.

Regeneration of dye-loaded MC

Regeneration of the exhausted MC (adsorption system of 0.01 g MC and 20 mL 150 mg/L DFY solution) was carried out by two methods: the exhausted MC was soaked in 10 mL 0.01 mol/L NaOH solution for 1 h or was placed in a single-mode microwave device. The experimental equipment for the microwave regeneration of MC consists of a microwave magnetron of a maximum output power 800 W with 2,450 MHz (G80W23CSP-Z, China). Exhausted MC situated inside an evaporating dish was placed into the microwave oven and exposed to microwave heating for 5 min at 320, 480, 640 W, respectively. Then, the regenerated MC can be reused as adsorbent to adsorb the DFY from solution. The regeneration yield was calculated as the ratio of values of q_e before and after regeneration using NaOH treatment or microwave irradiation.

Results and discussion

Characterization of MC

Elemental composition

Element composition from elemental analysis and XRF analysis is listed in Table 1.

From Table 1, PC was carbon rich, and there were some inorganic elements confirmed by XRF analysis, such as Si, K, Ca, Fe, Mg, Al, S, P. Compared with PC, content of magnesium oxide in MC significantly increased while content of K_2O and Fe_2O_3 decreased, which indicated that magnesium element was coated onto the surface of PC.

FTIR analysis

Fourier transform infrared (FTIR) analysis was carried out to characterize the surface organic functional groups presented on these samples. The FTIR spectrum of PC and MC is shown in Fig. 1.

From Fig. 1, FTIR spectrum of PC and MC displayed a number of absorption peaks, reflecting the complex nature of the materials. The bands were due to different surface groups. A strong absorption peak at about 3,415 cm^{-1} was assigned to stretching vibration of hydroxyl functional groups including hydrogen bonding due to adsorbed water. The absorption band near 2,900 cm^{-1} corresponds to the C–H stretching vibration from the methyl and methylene groups. The band at 1,559 cm^{-1} can be assigned to aromatic C=C vibration. In the fingerprint region (below 1,500 cm^{-1}), the band near 1,425 cm^{-1} is attributed to O–H bending or C–O stretching vibration of phenol, while the peak at 1,384^{-1} is assigned to C–H bending in alkanes/alkyl groups (Liu et al. 2012). The absorption band which was not markedly resolved in the location of 1,200–1,300 cm^{-1} may be from C–O vibration in phenols. The sharp peak at 1,047 cm^{-1} was attributed to –C–O–C– stretching vibrations of polysaccharides or from the bending vibration of –C–OH. The peak near 874 cm^{-1} was characteristic of C–H bending vibration in a β-glucosidic linkage (Ozcimen and Karaosmanoglu 2004). Another band was found at about 800 cm^{-1}, which was expected to be associated with the out-of-plane bending mode of O–H. The peak at 802 cm^{-1} and sharp peak at 462 cm^{-1} were also contribution of the adsorption from O–Si–O, indicating the presence of amounts of silica. This result was consistent with the higher content of SiO_2 for PC.

Table 1 Element composition of PC and MC (%)

Element	Al_2O_3	CaO	Cl	Fe_2O_3	K_2O	MgO	MnO
PC	1.17	15.51	3.18	6.806	14.82	3.22	0.233
MC	0.92	13.44	0.642	4.887	3.03	35.4	0.172
Element	P_2O_5	SO_3	SiO_2	TiO_2	N	C	H
PC	5.04	2.42	42.2	0.184	0.85	63.11	1.57
MC	5.42	2.26	32.1	0.1	0.77	60.42	1.78

Compared to PC, there was a sharp and strong peak at 3,698 cm^{-1} in MC, which was from O–H vibration from $Mg(OH)_2$. Another change was the peak (from hydroxyl functional groups) shifted (from 3,415 to 3,381 cm^{-1}). This also showed that magnesium hydroxide existed on the surface of PC. The observed spectra showed that MC consisted of several surface functional groups, which contributed to its color removal efficiency.

XRD analysis

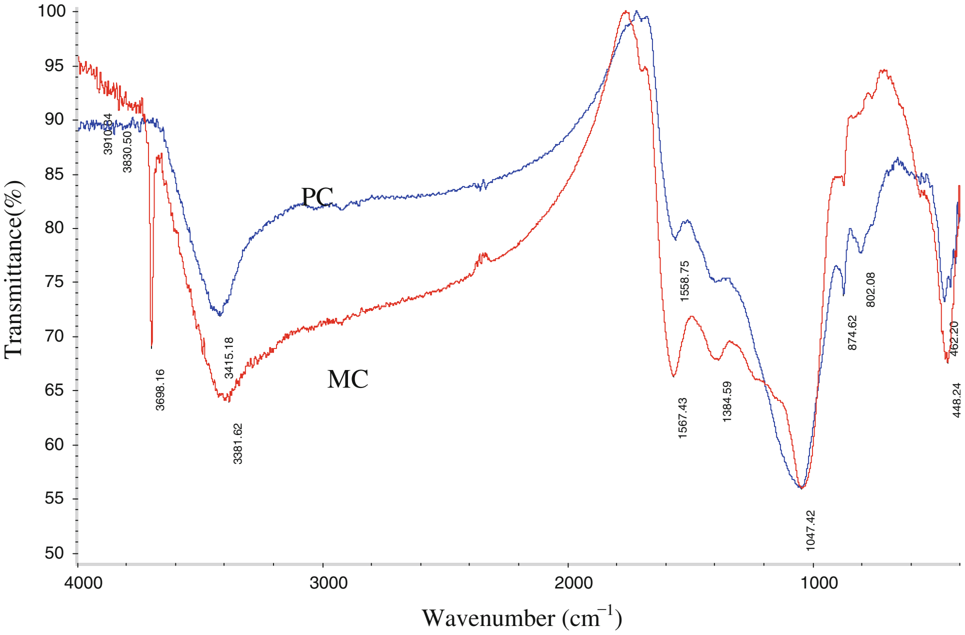
Powder XRD patterns for PC and MC are shown in Fig. 2. From Fig. 2, the peaks at $2\theta = 20°–30°$ referred to the stacking structure of aromatic layers (graphite 002), and the broadening originated from the small dimensions of crystallites perpendicular to aromatic layers (Takagi et al. 2004). Sharp and non-labeled peaks in PC indicated miscellaneous inorganic components. The greater prevalence of these peaks was consistent with the higher content of SiO_2, CaO, K_2O, Fe_2O_3. The sharp and strongest peak at $2\theta = 26°$ originated from crystalline SiO_2. The X-ray diffraction peak confirmed that PC possessed a heterogeneous surface. For MC, strength of peak at $2\theta = 26°$ became weak and a new peak at $2\theta = 38°$ appeared, which was from MgO contribution. This also showed that magnesium element was successfully coated onto surface of MC and there is new phase in the solid surface. The peak intensity of K_2O and Fe_2O_3 for MC decreased, and this was consistent with the lower contents of K_2O and Fe_2O_3 in MC.

Adsorption study

Effect of solution pH on adsorption

DFY is an anionic dye, which exists in aqueous solution in the form of negatively charged ions. As a charged species,

Fig. 1 FTIR of PC and MC



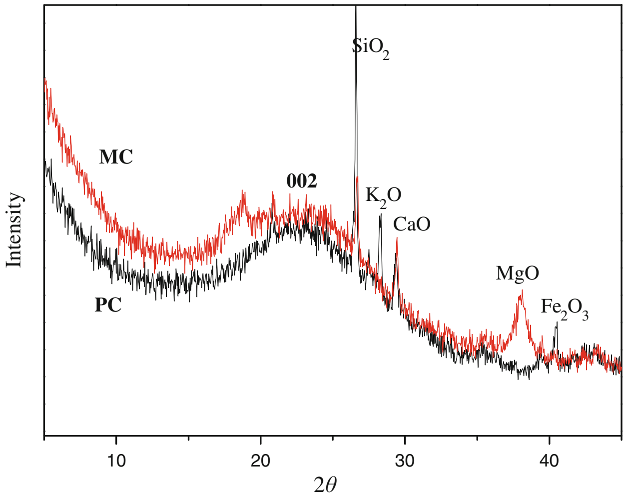


Fig. 2 XRD pattern of PC and MC

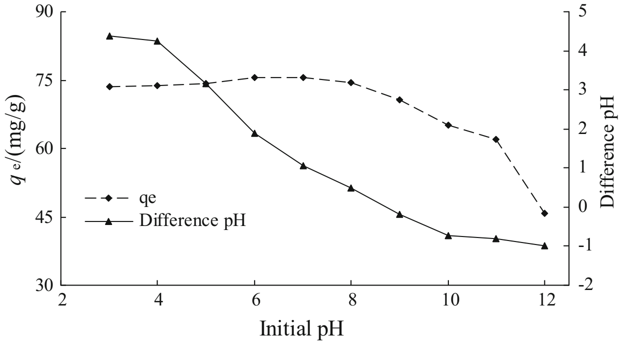


Fig. 3 The effect of initial pH of solution on adsorption and △pH between final pH and initial pH ($T = 293$ K, $c_0 = 50$ mg/L)

the degree of its adsorption onto the adsorbent surface is primarily influenced by the surface charge on the adsorbent, which in turn is influenced by the solution pH. Figure 3 shows the effect of pH on adsorption quantity.

The aqueous solution pH has a significant influence on the adsorptive uptake of dyes due to its effect on both the surface binding sites of the adsorbent and the ionization process of the dye molecule. From Fig. 3, it is observed that the value of q_e was insignificantly different at the solution pH within 4–8 and at pH 6–8 value of q_e was largest. At pH value over 8, adsorption capacity decreased. Apparently, the adsorption of DFY preferred at neutral or weak acid conditions. These results were consistent with pH_{PZC} 8.6 of MC. As the pH of DFY solution was near 6.0, the pH was not adjusted in the next experiment.

Change in solution pH before and after adsorption is also shown in Fig. 3. It was observed that change in pH is positive at initial solution pH below 8.0, while the change is negative at pH above 9.0. This trend was consistent with pH_{PZC} 8.6.

As the molar ratio of OH^- to Mg is 1.5 and Mg^{2+} is excess in the form of $Mg(OH)_2$, the surface of MC may be positive in solution. This enhances binding for anionic ions from solution.

Effect of salt concentration on adsorption

The dye wastewater has commonly higher salt concentration, and effects of salt concentration or ionic strength are important in the study of dye adsorption. Figure 4 shows the effect of various NaCl and Na_2SO_4 concentrations on the values of q_e.

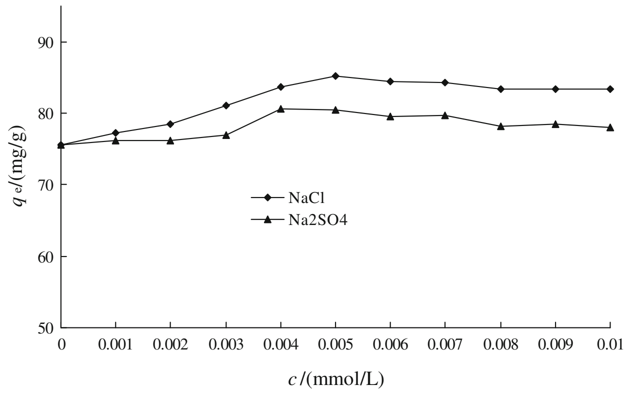


Fig. 4 Effect of NaCl and Na_2SO_4 concentration on DFY adsorption ($T = 293$ K, $c_0 = 50$ mg/L)

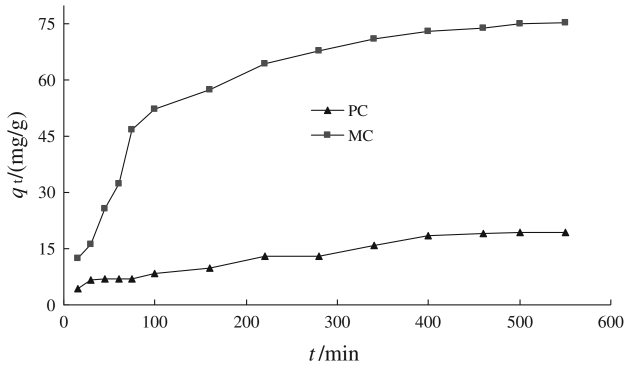


Fig. 5 Effect of contact time on adsorption ($c_0 = 50$ mg/L)

In Fig. 4, it is shown that the increase in the salt concentration resulted in an increase in values of q_e. Over 0.004 mol/L of salt concentration, the values of q_e decreased. This result showed that MC can be used to remove DFY from salt solution with some content.

The pHzpc of MC was estimated to be 8.5 and the equilibrium values of pH of solution were near 8.0, which means that the pH of the solution is less than pHzpc. Thus, MC as a positive surface attracted the negatively charged DFY molecules. Theoretically, when the electrostatic interaction between the adsorbent surface and the adsorbate ions is attractive, an increase in ion strength will decrease adsorption. However, the experimental results from this study did not follow this convention, as the adsorption capacity was enhanced by salt addition. This may be attributed to the presence of non-electrostatic forces, such as hydrogen bond and dispersive interaction. These forces were enhanced with increasing ion strength, which screened the electrostatic interaction and resulted in the constant adsorption capacity of MC for dye molecules.

It was also seen that the effect of Na_2SO_4 was smaller than that NaCl at same salt concentration. This may be explained by the effect of ionic strength. As there were higher ionic strength for Na_2SO_4 solution with same concentration of NaCl, the active coefficient decreased, and this resulted in decrease in the active concentration of dye in solution and active site on the surface of MC.

Effect of contact time on adsorption

The values of q_t at different contact time (t) for PC and MC are shown in Fig. 5, respectively.

From Fig. 5, both the kinetic curves showed that a three-stage kinetic behavior was evident: a rapid initial adsorption over 100 min, followed by a longer period of much slower uptake (400 min) and gradual equilibrium time. The first phase was the instantaneous adsorption stage or external surface adsorption. The second and third phases were the gradual adsorption stage, and finally DFY uptake reached equilibrium.

It was also seen that adsorption capacity of MC for DFY was significantly larger than that of PC. So it was concluded that the adsorption capacity of PC can effectively remove DFY through magnesium hydroxide coating.

The effect of equilibrium DFY concentration on adsorption

Adsorption isotherm studies were conducted in initial DFY concentration ranges of 30–200 mg/L. The effect of the equilibrium concentration of DFY in the solutions on adsorption is shown in Fig. 6 (adsorption isotherm). As seen from Fig. 6, equilibrium uptake increased with the increasing DFY concentrations at the range of experimental concentration. This was a result of the increase in the driving force of the concentration gradient.

The bigger adsorptive capacity of DFY was also observed in the higher temperature range. This was due to the increasing tendency of dye ions to adsorb from the

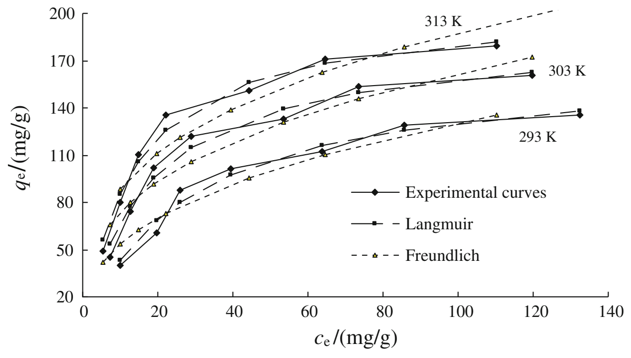


Fig. 6 Adsorption isotherms of DFY adsorption onto MC

Table 2 Regeneration yield at different conditions

Condition	320 W	480 W	640 W	0.01 mol/L NaOH
Yield/%	98.5	89.0	85.5	55.2

solution to the interface with increasing temperature. This indicated that the adsorption of DFY ions onto MC was endothermic in nature and adsorption was favored at higher temperature at the experimental condition.

Reusability of the adsorbent

The reusability of adsorbent is very important in industrial practice to make the wastewater treatment become economic. The regeneration of exhausted MC (DFY-loaded MC) was performed by chemical treatment using diluted NaOH solution as an elution solution and microwave irradiation. Table 2 lists the regeneration yields with different methods, respectively. From Table 2, the regeneration yield was 55 % by 0.01 mol/L solution. Furthermore, high regeneration yield was obtained through microwave irradiation, and it was up to 98 % using lower power of 320 W.

The application of microwave energy was proven to be superior to the use of conventional heating on accelerating reaction rates, improving yields, and selectively activating or suppressing reaction pathways. Microwave heating offers apparent advantages to adsorbent regeneration, including rapid and precise temperature control, small space requirements and greater efficiency (Yuen and Hameed 2009). Regeneration of first, second and third circles through microwave irradiation with power 320 W for 5 min was performed, and regeneration yields were 98.0, 88.7 and 85.1 %, respectively. The successive regeneration cycles reduced the microporosity of the adsorbent, and the yield of regeneration became smaller, but the change was insignificant. So MC can be considered as a reusable adsorbent. This result implied that the DFY-loaded MC can be reused as adsorbent to effectively remove DFY solution.

Adsorption equations modeling and determination of thermodynamic parameters

Adsorption isotherm modeling

The equilibrium isotherm model plays an important role in predictive results for analysis and design of adsorption systems. Langmuir and Freundlich isotherm models are common and often applied. Langmuir equation (Langmuir 1916):

$$q_e = \frac{q_m K_L c_e}{1 + K_L c_e} \tag{2}$$

where q_m is the q_e for a complete monolayer (mg/g), a constant related to adsorption capacity; and K_L is a constant related to the affinity of the binding sites and energy of adsorption (L/mg).

Freundlich equation (Freundlich 1906):

$$q_e = K_F c_e^{1/n} \tag{3}$$

where K_F and $1/n$ are the Freundlich constants related to the adsorption capacity and adsorption intensity of the adsorbent, respectively.

The relative parameters of each equation are obtained using least square sum (*SS*) between the calculated data and experimental data by nonlinear regressive analysis. The calculated expression of *SS* is as follows:

$$SS = \frac{\sum (q_c - q)^2}{n - 2} \tag{4}$$

where q_c is the predicted (calculated) quantity of DFY adsorbed onto MC according to adsorption models, q is the experimental data, and n is number of experimental points.

If higher values of R^2 and lower values of *SS* are obtained, the model is better to predict the experimental data.

The relative constants from the Langmuir and Freundlich models, the determined coefficients (R^2) and values of error (*SS*) are presented in Table 3. To assess the different isotherms and how they compare to experimental results, the theoretical plots for two models are also presented with the experimental data for the adsorption of DFY in Fig. 6.

From Table 3, values of q_m, the adsorption capacity for DFY removal, were 167.5, 187.3, 205.5 mg/g at 293, 303, 313 K, respectively, while values of K_L were 0.0352, 0.0548, 0.0710 mg/L at different temperature. For parameters of Freundlich, values of K_F were 42.1, 33.4, 22.1 at 293, 303, 313 K, respectively, while values of $1/n$ were 0.325, 0.343, 0.386 at various conditions.

It is evident from Fig. 6 and Table 3 that the equilibrium data were better represented by the Langmuir isotherm equation than by the Freundlich equation. The parameters of q_m, K_L and $1/n$ became larger with increase in temperature while parameter of K_F decreased. This indicated the homogeneous nature of MC where each dye molecule/MC adsorption had equal activation energy and the formation of

Table 3 Parameters of adsorption isotherm models for DFY adsorption

Isotherm constants	Temperature/K		
	293	303	313
Langmuir			
K_L (L/mg)	0.0352 ± 0.0054	0.0548 ± 0.0076	0.0710 ± 0.0084
q_m (mg/g)	167.5 ± 9.2	187.3 ± 8.3	205.5 ± 7.5
R^2	0.975	0.978	0.984
SS	35.7	45.6	44.4
Freundlich			
K_F	42.1 ± 8.9	33.4 ± 7.6	22.1 ± 5.4
$1/n$	0.325 ± 0.054	0.343 ± 0.056	0.386 ± 0.058
R^2	0.898	0.902	0.916
SS	282.3	205.6	122.6

monolayer coverage of dye molecules on the surface. The values of $1/n$ $(0.1 < 1/n < 1)$ indicated a favorable adsorption of DFY at experimental conditions (Aksu 2002).

Thermodynamic parameters of adsorption

The free energy change (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^0) were determined according to equilibrium data. The apparent equilibrium constant (K_c') of the adsorption is defined as (Aksu 2002):

$$K_c' = \frac{c_{a,d,e}}{c_e} \tag{5}$$

where $c_{ad,e}$ is the concentration of DFY on the adsorbent at equilibrium (mg/L). The value of K_c' can be obtained with the lowest experimental DFY concentration. The K_c' value is used o determine the Gibbs free energy change of adsorption (ΔG^0).

$$\Delta G^o = -RT\mathrm{In}K_c' \tag{6}$$

Assume that enthalpy and entropy are not independent on temperature during adsorption process. The change in enthalpy (ΔH^0) and entropy (ΔS^0) can be obtained from the slope and intercept of a van't Hoff equation of ΔG^0 versus T:

$$\Delta G^o = \Delta H^o - T\Delta S^o \tag{7}$$

where ΔG^o is standard Gibbs free energy change, J; R is universal gas constant, 8.314 J/mol K, and T is absolute temperature, K.

The thermodynamic parameters are listed in Table 4.

From Table 4, the negative values of ΔG^o were due to the fact that the adsorption processes were spontaneous. The increase in the absolute value of ΔG^o as temperature rises indicated that the affinity of DFY on MC was higher at high temperatures. The positive value of ΔH^o indicated the endothermic nature of the process, whereas the positive ΔS^o value confirmed the increased randomness at the solid–solute interface during adsorption. The low value of ΔS^o also indicates that no remarkable change in entropy occurs during adsorption process.

Table 4 Thermodynamic parameters of DFY adsorption

Thermodynamic parameters	Temperature/K		
	293	303	313
ΔG^0 (kJ/mol)	−1.73	−2.87	−4.04
ΔH^0 (kJ/mol)		32.16	
ΔS^0 (kJ/mol K)		0.115	

Conclusion

Magnesium hydroxide/pyrolytic bio-char composite (MC) prepared by chemical precipitation was characterized using FTIR, XRD, XFS, etc. The property of DFY adsorption onto MC was studied. Several factors, such as pH, contact time, salt concentration and equilibrium dye concentration, were investigated. Adsorption was favored at pH 6–8 and salt coexisted in solution slightly enhanced adsorption capacity. The equilibrium data were better fitted by Langmuir model, and the adsorption capacity was up to 167.5 ± 9.2 mg/g at 293 K. The process was spontaneous and endothermic in nature from thermodynamic parameters. The regeneration was effective by microwave irradiation and the exhausted MC can be reused after microwave irradiation.

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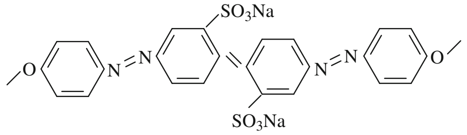
Appendix

The formula of DFY is as follows:



References

Aksu Z (2002) Determination of the equilibrium, kinetic and thermodynamic parameters of the batch biosorption of nickel(II) ions onto *Chlorella vulgaris*. Process Biochem 38(1):89–99

Arami-Niya A, Abnisa F, Shafeeyan M, Wan Daud WMA, Sahu JN (2012) Optimization of synthesis and characterization of palm shell-based bio-char as a by-product of bio-oil production process. Bioresources 7(2):246–264

Bhatnagar A, Sillanpaa M (2010) Utilization of agro-industrial and municipal waste materials as potential adsorbents for water treatment: a review. Chem Eng J 157(2–3):277–296

Bridgwater AV (2012) Review of fast pyrolysis of biomass and product upgrading. Biomass Bioenerg 38(1):68–94

Ding CS, Zeng HM, Fu J, Huang Y, Peng F, Xu ZR (2011) Study on the preparation and adsorption capability concerning Cd^{2+} of magnesium salt modified sand. J Lanzhou Uni (Nat Sci) 47(2):122–125 (in Chinese)

Eren E, Afsin B, Onal Y (2009) Removal of lead ions by acid activated and manganese oxide-coated bentonite. J Hazard Mater 161(2–3):677–685

Eren E, Tabak A, Eren B (2010) Performance of magnesium oxide-coated bentonite in removal process of copper ions from aqueous solution. Desalination 257(1–3):163–169

Freundlich HMF (1906) Uber die adsorption in lasungen. Z Phys Chem 57:385–470

Gupta VK, Suhas (2009) Application of low cost adsorbents for dye removal: a review. J Environ Manage 90(8):2313–2342

Han RP, Wang Y, Zhao X, Wang YF, Xie FL, Cheng JM, Tang MS (2009a) Adsorption of methylene blue by phoenix tree's leaf powder in fixed-bed column: experiments and prediction of breakthrough curves. Desalination 245(1–3):284–297

Han RP, Zou LN, Zhao X, Xu YF, Xu F, Li YL, Wang Y (2009b) Characterization and properties of iron oxide-coated zeolite as adsorbent for removal of copper (II) from solution in fixed bed column. Chem Eng J 149(1–3):123–131

Han RP, Wang Y, Sun Q, Wang LL, Song JY, He XT, Dou CC (2010) Malachite green adsorption onto natural zeolite and reuse by microwave irradiation. J Hazard Mater 175(1–3):1056–1061

Ioannidou O, Zabaniotou A (2007) Agricultural residues as precursors for activated carbon production: a review. Renew Sust Energy Rev 11(9):1966–2005

Jones DA, Lelyveld TP, Mavrofidis SD, Kingman SW, Miles NJ (2002) Microwave heating applications in environmental engineering: a review. Resour Conserv Recycl 34(1):75–90

Langmuir I (1916) The constitution and fundamental properties of solids and liquids. J Am Chem Soc 38:2221–2295

Lee JW, Kidder M, Evans BR, Paik S, Buchanan Iii AC, Garten CT, Brown RC (2010) Characterization of biochars produced from corn stovers for soil amendment. Environ Sci Technol 44(20):7970–7974

Liu XT, Quan X, Bo LL, Chen S, Zhao YZ (2004) Simultaneous pentachlorophenol decomposition and granular activated carbon regeneration assisted by microwave irradiation. Carbon 42(2):415–422

Liu YL, Zhao XR, Li JL, Ma D, Han RP (2012) Characterization of bio-char from pyrolysis of wheat straw and its evaluation on methylene blue adsorption. Desalin Water Treat 46(1–3): 115–123

Mohan D, Rajput S, Singh VK, Steele PH, Pittman CU Jr (2011) Modeling and evaluation of chromium remediation from water using low cost bio-char, a green adsorbent. J Hazard Mater 188(1–3):319–333

Ozcimen D, Karaosmanoglu F (2004) Production and characterization of bio-oil and biochar from rapeseed cake. Renew Energy 29(5):779–787

Qiu YP, Zheng ZZ, Zhou ZL, Sheng GD (2009) Effectiveness and mechanisms of dye adsorption on straw-based biochar. Bioresour Technol 100(21):5348–5351

Robinson T, McMullan G, Marchant R, Nigam P (2001) Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. Bioresour Technol 77(3):247–255

Sun JX, Wang HZ, Sun BW (2011) Study on adsorption of weak acid red B on activated carbon modified by magnesium salt. Chin J Environ Eng 5(2):261–266 (in Chinese)

Takagi H, Maruyama K, Yoshizawa N, Yamadab Y, Sato Y (2004) XRD analysis of carbon stacking structure in coal during heat treatment. Fuel 83(17–18):2427–2433

Wan Ngah WS, Hanafiah MAKM (2008) Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: a review. Bioresour Technol 99(10):3935–3948

Wang SB, Peng YL (2010) Natural zeolites as effective adsorbents in water and wastewater treatment. Chem Eng J 156(1):11–24

Wu YJ, Zhang LJ, Gao CL, Ma JY, Ma XH, Han RP (2009) Adsorption of copper ions and methylene blue in single and binary system on wheat straw. J Chem Eng Data 54(12): 3229–3234

Yuen FK, Hameed BH (2009) Recent developments in the preparation and regeneration of activated carbons by microwaves. Adv Colloid Interface Sci 149(1–2):19–27

Zhang LJ, Ma D, Mao GY, Zhang MM, Han RP (2011) Adsorption of neutral red from solution by Bio-chars produced from fast pyrolysis of wheat straw. Adv Mater Res 322:72–76

Zhao L, Zou WH, Zou LN, He XT, Song JY, Han RP (2010) Adsorption of methylene blue and methyl orange from aqueous solution by iron oxide-coated zeolite in fixed bed column: predicted curves. Desalin Water Treat 22(1–3): 258–264

Zhu Y, Zhang H, Zeng H, Liang M, Lu R (2012) Adsorption of chromium (VI) from aqueous solution by the iron (III)-impregnated sorbent prepared from sugarcane bagasse. Int J Environ Sci Technol 9(3):463–472

Zou WH, Han RP, Chen ZZ, Shi J, Liu HM (2006) Characterization and properties of manganese oxide coated zeolite (MOCZ) as adsorbent for removal of copper(II) and lead(II) ions from solution. J Chem Eng Data 51(2):534–541

Zou WH, Zhang JH, Li K, Han P, Han RP (2009) Characterization of manganese oxide and adsorption of copper and lead from aqueous solutions. Adsorpt Sci Technol 27(6):549–565