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Congo Red Adsorption Capacity of Lignocellulosic Biomass by Sodium Hydroxide Treatment

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To investigate the enhancement of Congo red adsorption capacity of lignocellulosic biomass with sodium hydroxide treatment, five various lignocellulosic biomasses were employed and respectively treated by different concentration of NaOH to remove congo red from aqueous solution. Results showed that NaOH treatment is an effective method for enhancement of congo red adsorption capacity of the biomasses. The capacity of sorghum stalk was the most considerably enhanced by NaOH treatment in comparison to that of other biomasses. Fourier transform infrared spectroscopy showed that the C=O bond of carboxylic acid or its ester in biomasses was destroyed and the -OH and -NH bonds in biomasses were varied by NaOH treatment. Scanning electron microscopy demonstrated that structure of the biomasses was breakdown after NaOH treatment. It is deduced that NaOH treatment considerably enhanced the congo red adsorption capacity of lignocellulosic biomass is due to destruction of its structure and variation of its functional groups.

Keywords: Adsorption, Lignocellulosic biomass, Sodium hydroxide treatment, Congo red.

INTRODUCTION

There are more than 100,000 synthetic dyes available commercially and over 1 million ton dyes are produced per year[1,2]. These synthetic dyes include several structural varieties such as azo, basic, acidic, disperse, reactive and anthraquinone dyes[3]. A major class of all dyes is azo dyes which represent about 70 % on weight basis[2]. Congo red (CR), a benzidine-based anionic azo dye has been widely used in textiles, rubber, printing and plastics industries which release amounts of congo red contaminated wastewater. Congo red has been known to cause allergic reactions and to be metabolized to benzidine which is a human carcinogen. Besides having possible harmful effects, the dye in water is aesthetically unpleasant. Thus, congo red contaminated wastewater is worrying for both toxicological and aesthetical reasons[4-7]. Yet, congo red contaminated wastewater is hardly treated owing to the complex aromatic structure of congo red, providing the dye physico-chemical, thermal and optical stability[8].

Adsorption is a promising technique for removal of dye from wastewater due to its natures of flexibility and simplicity of design, ease of operation and insensitivity of toxic pollutants[9,10]. Moreover, lignocellulosic biomass has been extensively studied as alternative adsorbent for removal of dyes since it is freely and abundantly[11-15]. Lignocellulosic biomass is mainly composed of three types of polymers, namely cellulose, hemicellulose and lignin. These polymers contain functional groups such as hydroxyl, carboxyl and others, which could form active sites for adsorption of dyes on the biomass[16,17]. However, since the organization and interaction between these polymeric structures, lignocellulosic biomass is integrity, tough and inert thus causing its dye adsorption capacity is low[17-19]. Thus, to enhance the dye adsorption capacity of lignocellulosic biomass, the biomass would be modified before being applied for the decontamination of dyes[19-22]. Sodium hydroxide treatment is an effective method for chemical modification of lignicellulosic biomass[9,16,18,23]. Sodium hydroxide breaks the covalent association between lignocellulose components, specifically targets hemicellulose acetyl groups and lignin-carbohydrate ester linkages and removes natural fats and waxes from the biomass. Moreover, this treatment has influences on morphology of biomass. Sodium hydroxide treatment has been employed to chemically modify lignocellulosic biomass for enhancement of its dye adsorption capacity[9,19,22,24]. Sodium hydroxide treated saw dust[24], NaOH treated rejected tea[19] and NaOH treated rice husk[9] were excellent alternative absorbents for the removal of brilliant green, methylene blue and crystal violet from aqueous solution, respectively. However, congo red adsorption using NaOH treated lignocellulosic biomass and mechanism of NaOH treatment for enhancement of congo red adsorption capacity of the biomass has never been specifically investigated in previous literature.

This study is attempting to explore the possibility of utilizing NaOH treated lignocellulosic biomass for the removal of congo red from aqueous solution by performing batch experiments. Five various lignocellulosic biomasses involving cassava residue, rice straw, sorghum stalk, sesame stalk and saw dust were, respectively modified by NaOH treatment for enhancement of their congo red adsorption capacity. Moreover, to explore the mechanism of NaOH treatment for enhancement of congo red adsorption capacity of lignocellulosic biomasses, functional groups and morphological characteristics of the biomasses before and after NaOH treatment were evaluated by Fourier transform infrared spectroscopy (FTIR) and scanning electron microscope (SEM), respectively.

EXPERIMENTAL

Fresh biomass of rice straw, sorghum stalk and sesame stalk was respectively collected from their natural habitats in the farmland, Wuxi, China. Cassava residue is a lignocellulosic waste which was generated in the distilling step of cassava-based ethanol production and provided by Yong Xiang Ethanol Co., Ltd., Wujiang, China. Saw dust was collected from a saw mill near Jiangnan University, Wuxi, China. The biomass was washed and dried at 105 °C until constant weight was obtained. The dried biomass was milled to a fine powder and passed through 80-mesh screen. The powdered biomass was stored in an airtight plastic container and used for experiments. Lignocellulose components of the biomass were determined according to Van Soest's method[25,26] and showed in Table-1.

Congo red (C.I. 22120, m.f.: $C_{32}H_{22}N_6Na_2O_6S_2$, m.w.: 696.68, λ_{max}: 495 nm) was obtained from Shanghai Yuming Industrial Co., Ltd., Yuanhang Reagent Factory, China. The stock solution of congo red (1000 mg/L) was prepared in sodium phosphate buffer (50 mM, pH 8.5). All working solutions were prepared by diluting the stock solution with sodium phosphate buffer (50 mM, pH 8.5) to the desired concentration. All reagents used were of analytical grade.

Sodium hydroxide treatment of biomass: Treatment of all biomasses was conducted at the following alkali levels: 0, 5, 10 and 20 g NaOH per 100 g dried biomass with 5 % (w/w) the biomass concentration at 30 °C in batch reactors on a rotary shaker at 200 rpm for 24 h[23]. Treated biomass was separated by filtering slurries through filter cloth and washed by distilled water till the pH value of eluate was in the range of 6.8 to 7.2. Then the treated biomass was dried at 105 °C until constant weight was obtained. The dried biomass was milled to a fine powder and passed through 80 mesh screen. The powdered biomass was stored in an airtight plastic container and used as adsorbent for experiments.

Adsorption experiments in batch: Batch adsorption experiments were carried out in a series of 250 mL Erlenmeyer flasks mixed with 50 mL of congo red solution and 0.1 g adsorbent. The flasks were shaken on a rotary shaker with 30 °C at 150 rpm for 240 min to obtain equilibrium of the adsorption. After the adsorption, the flasks were withdrawn from the shaker and the residual dye concentration in the mixture was analysed by centrifuging (4500 × g, 10 min) the mixture and then measuring value of the supernatant at the wavelength of maximum absorbance with a UV/visible spectrometry (Model UV2100, Unic, Shanghai). The amount of dye adsorbed per unit adsorbent (mg dye per g adsorbent) was calculated according to eqn. 1[11,27]. The experiments were conducted by varying the congo red concentration (50-400 mg/L) to calculate the maximum adsorption capacity (q_m, mg/g) of the adsorbent *via* fitting experimental adsorption data with the Langmiuir model (eqn. 2)[12,28]. Experiments were repeated thrice and average values were used for calculations.

$$q_e = \frac{(C_0 - C_e)}{m} \times V \quad (1)$$

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \left(\frac{1}{K_a q_m}\right) \quad (2)$$

where C_0 (mg/L) is initial congo red concentration, C_e (mg/L) is congo red concentration in the mixture at equilibrium time, V (L) is the volume of solution and m (g) is the mass of adsorbent. q_e (mg/g) is the amount of congo red adsorbed per unit of adsorbent at equilibrium time (mg/g), q_m (mg/g) is the maximum adsorption capacity calculated by the model, K_a is a Langmuir constant.

Fourier transform infrared spectroscopy analysis: Untreated (0 % NaOH treated) biomass and 20 % NaOH treated biomass were characterized by Fourier transform infrared spectroscopy (FTIR) (Nicolet Nexus 470, Thermo Electro Co., USA). Discs were prepared by first mixing powered sample with potassium bromide in an agate mortar. Spectra were recorded by averaging 32 scans from 4,000 to 400 cm^{-1}. The background spectrum of pure potassium bromide was subtracted from the sample spectrum.

Scanning electronic microscope analysis: A scanning electron microscope (SEM) (FEI Quanta 200, Holland) was used for the characterization of morphological structure of untreated biomass and 20 % NaOH treated biomass.

RESULTS AND DISCUSSION

Effect of congo red concentration and NaOH concentration on adsorption amount: Effect of congo red concentration on adsorption amount of congo red for various adsorbents was investigated in the range of 50 to 400 mg/L which was shown in Fig. 1. The increase of congo red concentration resulted in increase of adsorption amount of congo red.

TABLE-1
COMPOSITION OF LIGNOCELLULOSIC BIOMASSES USED IN THIS WORK

Lignocellulosic biomass	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Cassava residue	31.46 ± 0.63	10.49 ± 0.20	20.19 ± 0.22
Rice straw	30.09 ± 0.72	25.33 ± 0.87	9.50 ± 0.06
Sorghum stalk	29.05 ± 0.67	22.52 ± 0.34	12.11 ± 0.18
Sesame stalk	40.34 ± 0.85	12.64 ± 0.49	17.48 ± 0.13
Saw dust	42.49 ± 1.20	13.56 ± 0.70	26.05 ± 0.53

This is attributed to enhance the driving force to overcome the resistance to the mass transfer of congo red between the aqueous phase and the solid phase[29]. Also from Fig. 1, it was found that the congo red uptake capacity of biomass was considerably enhanced by NaOH treatment. Moreover, the adsorption amount of congo red increased with increasing of NaOH concentration ranged from 0 to 20 %. Taking the congo red concentration was 400 mg/L for example, 20 % NaOH treated biomass demonstrated one to two folds higher adsorption amount of congo red than that of the untreated analogs. This result is in agreement with those reported previously by other researchers for adsorption of other dyes by various NaOH treated lignocellulosic biomasses[9,19,24].

Congo red adsorption capacity of biomass and NaOH treated biomass: To further investigate the effect of NaOH treatment on congo red adsorption capacity of the biomass, adsorption isotherm of the biomasses treated by different concentration of NaOH was fitted by the Langmuir model to give an idea of their maximum adsorption capacity on the basis of data from Fig. 1. As shown in Fig. 2, plots of C_e/q_e against C_e for different adsorbents showed excellent linearity. The correlation cofficient (R^2) of the plots was more than 0.95 (Table-2), indicating that the adsorption data fitted well to the Langmuir model. This observation is consistent with those reported previously by other researchers for the adsorption of congo red by various materials[4,8,10,30,31]. It is suggested that congo

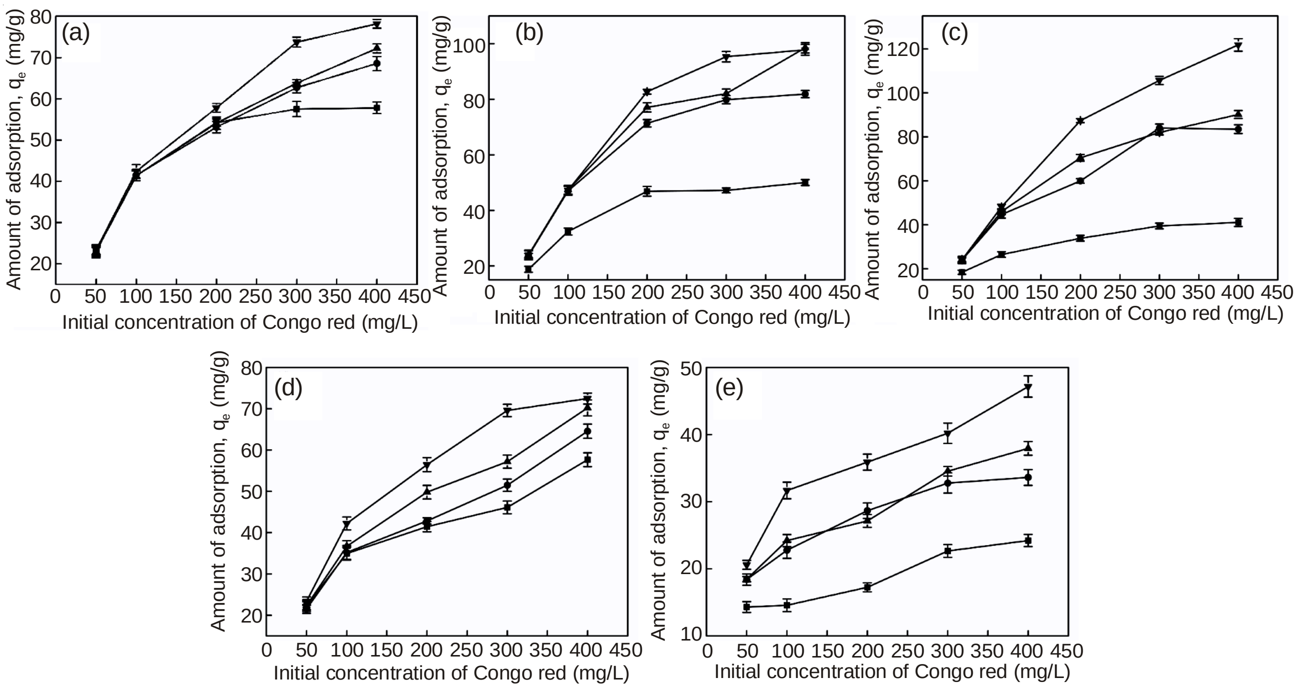

Fig. 1. Effects of Congo red concentration and NaOH concentration on the adsorption amount of adsorbents. (a, b, c, d, and e indicates cassava residue, rice straw, sorghum stalk, sesame stalk, and saw dust, respectively). (■ ● ▲ ▼ indicates 0 % NaOH treatment, 5 % NaOH treatment, 10 % NaOH treatment, and 20% NaOH treatment, respectively)

TABLE-2
PARAMETERS OF LANGMUIR MODEL FOR THE ADSORPTION OF CONGO RED ON ADSORBENTS USED IN THIS WORK

Adsorbent	Maximum adsorption capacity, q_m(mg/g)	K_a	R^2
Untreated cassava residue	59.17	0.14	0.9999
5 % NaOH treated cassava residue	70.42	0.06	0.9917
10 % NaOH treated cassava residue	74.07	0.06	0.9873
20 % NaOH treated cassava residue	81.97	0.06	0.9891
Untreated rice straw	53.19	0.05	0.9986
5 % NaOH treated rice straw	84.03	0.15	0.9996
10 % NaOH treated rice straw	98.04	0.10	0.9864
20 % NaOH treated rice straw	101.01	0.14	1.0000
Untreated sorghum stalk	44.25	0.04	0.9957
5 % NaOH treated sorghum stalk	86.96	0.07	0.9813
10 % NaOH treated sorghum stalk	91.74	0.10	0.9950
20 % NaOH treated sorghum stalk	125.00	0.11	0.9948
Untreated sesame stalk	57.14	0.04	0.9648
5 % NaOH treated sesame stalk	65.79	0.03	0.9531
10 % NaOH treated sesame stalk	71.94	0.04	0.9704
20 % NaOH treated sesame stalk	75.19	0.07	0.9934
Untreated saw dust	26.46	0.02	0.9615
5 % NaOH treated saw dust	35.71	0.04	0.9952
10 % NaOH treated saw dust	40.16	0.03	0.9721
20 % NaOH treated saw dust	47.85	0.04	0.9806

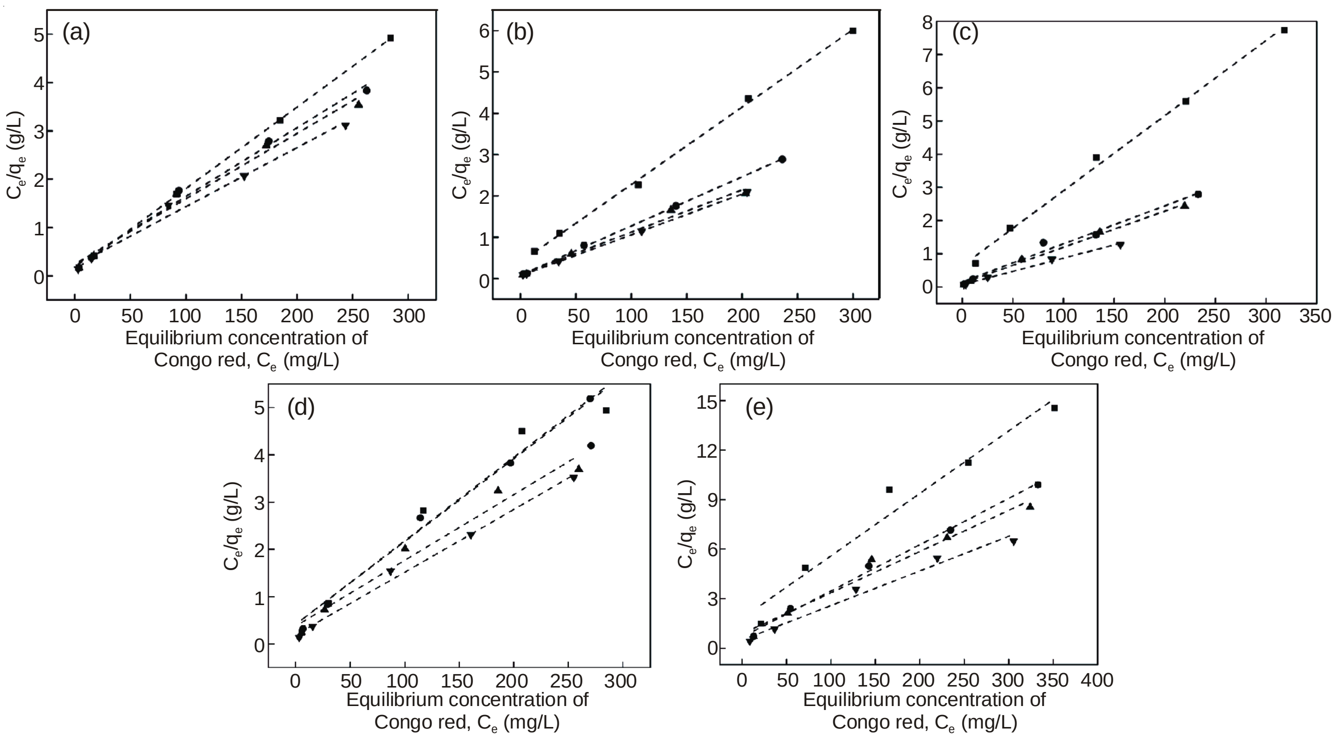

Fig. 2. Langmuir isotherm profiles for the adsorption of Congo red on various adsorbents. (a, b, c, d, and e indicates cassava residue, rice straw, sorghum stalk, sesame stalk, and saw dust, respectively.). (■ ● ▲ ▼ indicates 0 % NaOH treatment, 5 % NaOH treatment, 10 % NaOH treatment, and 20 % NaOH treatment, respectively)

red adsorption on the surface of the adsorbents is monolayer adsorption *i.e.* an active site was once occupied by an adsorbate molecule. Moreover, from the Table-2, it is found that maximum adsorption capacity (q_m) increased with increasing of NaOH concentration. It is suggested that NaOH treatment was an effective method for enhancing congo red adsorption capacity of lignocellulosic biomass. Among the five various biomasses used in this work, congo red adsorption capacity of sorghum stalk was the most considerably enhanced by NaOH treatment, the capacity of 20 % NaOH treated sorghum stalk demonstrated about two folds higher than that of untreated sorghum stalk.

Several studies have been investigated on removal of congo red from aqueous solution using various adsorbents. Table-3 summarized the comparison of the maximum congo red adsorption capacities of various adsorbents whose adsorption isotherm is well agreed with the Langmuir model. It is showed that the NaOH treated biomass has moderately higher adsorption capacity of congo red than many of other reported adsorbents, indicating that the NaOH treated biomasses had a great potential to be used as adsorbents for the removal of congo red from aqueous solution. Moreover, the capacity of 20 % NaOH treated sorghum stalk was the best in this work and achieved by 125 mg/g.

FTIR spectra of biomass and NaOH treated biomass: Fig. 3 showed the FTIR spectra of five lignocellulosic biomasses involving cassava residue (Fig. 3a), rice straw (Fig. 3b), sorghum stalk (Fig. 3c), sesame stalk (Fig. 3d) and saw dust (Fig. 3e). Similar type of FTIR spectra of other lignocellulosic

TABLE-3
COMPARISONS OF MAXIMUM ADSORPTION CAPACITY OF CONGO RED ON VARIOUS ADSORBENTS

Adsorbent	Maximum adsorption capacity, q_m(mg/g)	Ref.
Cattail root	38.79	4
Ethylenediamine-modified wheat straw	68.60	6
Kaolin	5.44	8
N,O-carboxymethyl-chitosan	375.94	10
Chitosan	81.23	10
Cashew nut shell	5.18	11
Maghemite nanoparticles	208.33	30
Kazimierz-Juliusz coal impregnated with titanium oxide acetylacetonate (KJA/Ti)	52.00	31
Waste orange peel	22.44	34
Quaternary ammonium groups-grafted Sunflower	191.00	35
macauba palm cake	34.87	36
20 % NaOH-treated sorghum stalk	125.00	Present study
20 % NaOH-treated rice straw	101.01	Present study
20 % NaOH-treated cassava residue	81.97	Present study
20 % NaOH-treated sesame stalk	75.19	Present study
20 % NaOH treated saw dust	47.85	Present study

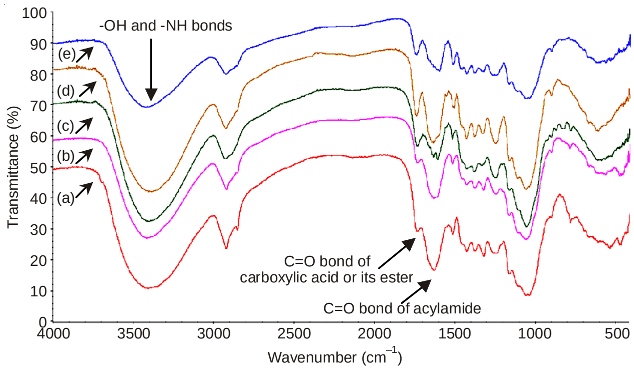

Fig. 3. FTIR of various lignocellulosic biomasses used in this work. (a, b, c, d, and e indicates cassava residue, rice straw, sorghum stalk, sesame stalk and saw dust, respectively)

biomasses has been reported in previous literature[12,15,32]. The FTIR spectra displayed a number of absorption bands, indicating the complex natures of the biomass. Notably, FTIR analysis indicated broad bands at 3500-3300 cm^{-1}, representing bonded -OH and -NH[12,15,33]. The band observed at 1750-1730 cm^{-1} was assigned to a carbonyl (C=O) bond of carboxylic acid or its ester[15,32]. The band observed at about 1630 cm^{-1} was assigned to a C=O bond of acylamide[33]. Previous reports demonstrated that the predominant interaction of congo red adsorption onto lignocellulosic biomass was hydrogen bond formed between the -OH, -NH, -C=O and -CONH$_2$ groups of the biomass and the -NH$_2$, -N=N- and -SO$_3$ groups of congo red molecules[7,10]. Fig. 4 showed that the major differences in FTIR spectra of the NaOH treated biomasses were the disappearance of carbonyl (C=O) bond of carboxylic acid or its ester, indicating that the carbonyl bond was destroyed by NaOH treatment. Moreover, as shown in Table-4, bands observed at about 3400 cm^{-1} shifted after NaOH treatment, indicating that bond energy of -OH and -NH was varied by NaOH treatment. Bands observed at about 1630 cm^{-1} of cassava residue, rice straw and sesame stalk shifted but that of sorghum stalk and saw dust did not shift, indicating that the influence of NaOH treatment on carbonyl (C=O) bond of acylamide was different in biomass species.

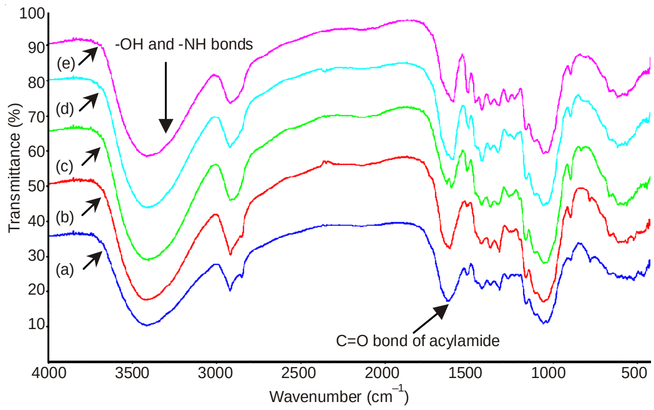

Fig. 4. FTIR of various lignocellulosic biomasses treated by 20 % NaOH (a, b, c, d, and e indicates cassava residue, rice straw, sorghum stalk, sesame stalk, and saw dust, respectively)

SEM micrograph of biomasses and NaOH treated biomasses: SEM examination of the five lignocellulosic biomasses before and after NaOH treatment gives further insight on the biomasses morphology and their modification during the treatment. As shown in Fig. 5(a), untreated biomasses had contact and smooth flat surface and exhibited rigid and connected structure. Morphological characteristic of the biomass was altered by NaOH treatment. Structure of NaOH treated biomasses was rugged and loosed and many cracks were observed (Fig. 5b). The SEM observations showed that the morphology of lignocellulosic biomass was dramatically changed by NaOH treatment, the initial connected structure was destroyed. The morphological modification induced by NaOH treatment is due to destruction of the covalent association between lignocellulose components and removal of natural fats and waxes from the biomasses[9].

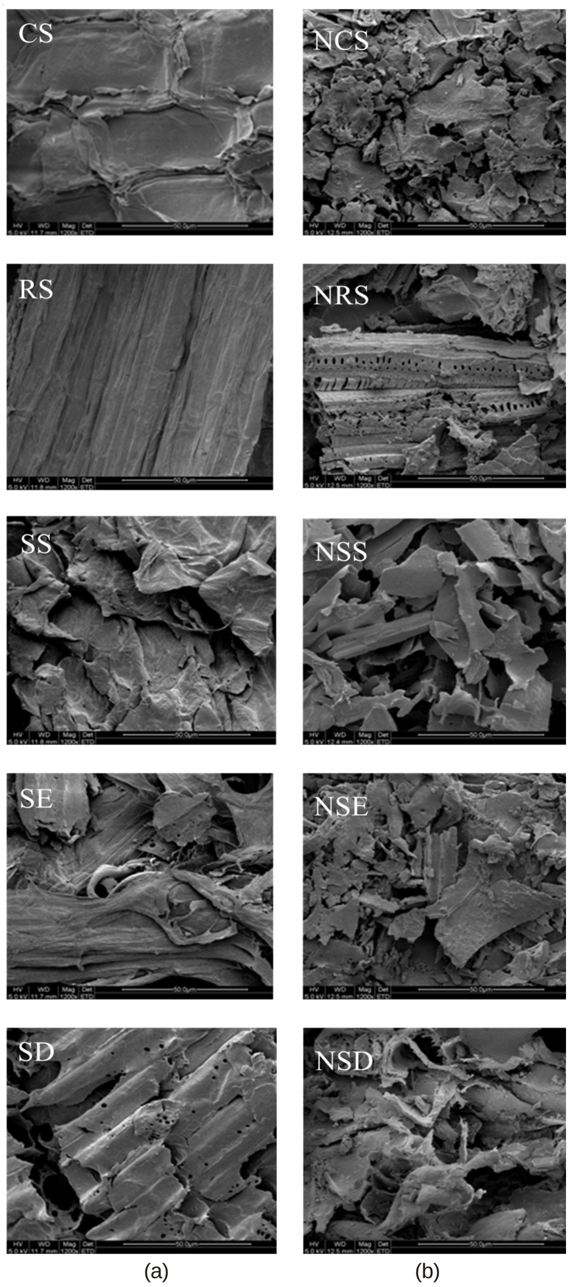

Fig. 5. SEM micrograph (magnification×1200) of lignocellulosic biomasses (a) and 20 % NaOH treated biomasses (b). CS, RS, SS, SE, SD indicates cassava residue, rice straw, sorghum stalk, sesame stalk, and saw dust, respectively. NCS, NRS, NSS, NSE, NSD indicates cassava residue, rice straw, sorghum stalk, sesame stalk, and saw dust treated by 20 % NaOH, respectively

TABLE-4
BAND OF FUNCTIONAL GROUPS IN FTIR SPECTRA OF UNTREATED BIOMASS AND NAOH TREATED BIOMASS

Biomass	Untreated biomass		20 % NaOH treated biomass	
	-OH and -NH band (cm^{-1})	C=O of acylamide group band (cm^{-1})	-OH and -NH band (cm^{-1})	C=O of acylamide group band (cm^{-1})
Cassava residue	3415	1629	3419	1632
Rice straw	3405	1631	3427	1614
Sorghum stalk	3413	1631	3407	1631
Sesame stalk	3406	1639	3403	1630
Saw dust	3407	1629	3415	1629

Mechanism of NaOH treatment for enhancement of congo red adsorption capacity of lignocellulosic biomass: The predominant interaction of congo red adsorption onto lignocellulosic biomass was hydrogen bond formed between -OH, -NH, -C=O and -$CONH_2$ groups of the biomass and -NH_2, -N=N- and -SO_3 groups of congo red molecules[7,10]. In the present study, congo red adsorption capacity of five various lignocellulosic biomasses was enhanced by NaOH treatment. FTIR analysis showed that the functional groups for congo red adsorption on the biomass were varied by NaOH treatment, notably the destruction of carbonyl bond (C=O) of carboxylic acid or its ester and variation of -OH and -NH bonds. Moreover, SEM analysis showed the initial connected structure of lignocellulosic biomass was considerably destroyed by NaOH treatment. Thus, it is deduced that NaOH treatment considerably enhanced the congo red adsorption capacity of lignocellulosic biomass is due to structural destruction of the biomass and variation of its functional groups.

Conclusion

This study showed that NaOH treatment is an effective method to enhance congo red adsorption capacity of lignocelluosic biomass. Sodium hydroxide treated lignocellulosic biomass is a promising adsorbent for the removal of congo red from aqueous solution. Among the tested biomasses in this work, congo red adsorption capacity of sorghum stalk is the most considerably enhanced by NaOH treatment. The maximum congo red adsorption capacity of 20 % NaOH treated sorghum stalk achieved by 125 mg/g. Analyses of FTIR and SEM implied that NaOH treatment considerably enhanced congo red adsorption capacity of lignocellulosic biomass is due to structural destruction of the biomass and variation of its functional groups.

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