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Sulfur fixation on bagasse activated carbon by chemical treatment and its effect on acid dye adsorption

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Abstract Heteroatoms are known to introduce specific surface functionalities that can enhance the adsorption properties of carbons. Sulfur fixation on bagasse-activated carbon was conducted by a low temperature chemical treatment with sulfuric acid followed by physical activation with CO_2 at 900 °C. The effect of sulfur fixation on the surface chemical properties of bagasse-activated carbons were investigated and on their subsequent acid dye removal (CIBA AB80) behavior. Surface chemical development were examined and followed using Fourier transform infrared spectroscopy (FTIR), heteroatom analysis and carbon surface acidity. Functional group stability with thermal treatment was also investigated. The textural properties of the activated carbons were characterized by nitrogen adsorption. Chemical pre-treatment and gasification was able to fix up to 0.2 wt% of sulfur on the activated carbon. Although the sulfur fixed by chemical treatment is low, this method introduced several advantages in comparison to fixation by thermal methods. The chemical method did not interfere with the textural development of the carbon, as found in thermal methods. In addition, the surface chemistry generated by these levels of sulfur groups was sufficient to increase the uptake of acid blue dyes by more than 700% based on adsorption capacities normalized by the surface area of the carbon.

Keywords Bagasse · Sulfur fixation · Activated carbon · Adsorption

1 Introduction

Dye effluents are not only aesthetic pollutants as far as their colors are concerned but they also interfere with light penetration in receiving bodies of water thereby disturbing the biological process. Furthermore dye effluents may contain chemicals which exhibits toxic effects towards microbial populations and can be toxic and/or carcinogenic to mammals (Reife 1993). Although various methods including chemical oxidation, biological treatment, coagulation-flocculation and membrane processes are available in treating dye waste water (Baclioglu and Arsan 2001; Juang et al. 1996), the use of activated carbons remains widely favored. Activated carbons exhibit amphoteric properties which enable them to adsorb both cationic and anionic dyes (Al-Degs et al. 2000; Corapcioglu and Huang 1987). However, the production cost of activated carbons remains high. This has attracted considerable research into low cost alternative materials for the production of activated carbon from agricultural wastes, such as apricot stones (Khalil and Girgis 1998), bamboo (Chan et al. 2008; Wu et al. 1999a), and plum kernels (Wu et al. 1999b). Among these researches, the control of the textural properties and in particular the surface chemistry of carbons to meet the needs of special application such as dye adsorption, have received considerable interest. Surface functional groups are expected to greatly modify surface characteristics and surface behavior of the carbon. These groups can originate from the precursor and production process. Surface modification by fixation of sulfur, nitrogen, hydrogen and other chemical groups in

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carbonaceous adsorbents have been used to provide a controlled developed of the surface chemistry of carbonaceous adsorbents (Valix et al. 2006; Zhang et al. 2005). Although the benefits of surface modifications are well documented (Krishnan and Anirudhan 2002), the current understanding of its effect on the adsorption process is limited. The modification of carbonaceous adsorbents to yield carbon–sulfur surface compounds have been conducted in a variety of carbon based solids including chars, activated carbon, carbon blacks and coals. These carbon–sulfur compounds are generally formed by heating the carbon in the presence of sulfur vapors (Sykes and White 1956), sulfurous gases such as hydrogen sulfide (Bansal and Gupta 1980), sulfur dioxide (Puri et al. 1968) and carbon disulfide (Puri and Hazra 1971). Carbonaceous solids containing sulfur or other pyrolytic sulfur have also been used to produce sulfur surfaced solids. Appreciable amounts of sulfur are usually taken up by the carbonaceous precursor, typically the range is between 6 to 50% by weight (Bansal and Gupta 1980). These sulfur surface compounds exhibit a wide range of properties including thermal and chemical stability. The sulfur compounds cannot be decomposed when heated at 1000 °C or extracted with solvents. This is with the exception of reaction with hydrogen between 500 and 700 °C, where sulfur compounds react to form hydrogen sulfide. Of particular interest is the enhanced metal uptake exhibited by adsorbents on which sulfur compounds have been fixed. Krishnan and Anirudhan (2002) have shown the introduction of sulfur based compounds into bagasse by exposure of the carbon to SO_2 and H_2S, during activation generated significantly enhanced heavy metal removal.

Although the merit of sulfur fixation in activated carbon has been demonstrated, the benefits of such high concentrations of sulfur in the carbon surface are not clear. An alternative technique using chemical treatment with sulfuric acid during carbonization was considered in this study to fix sulfur groups on the surface of activated bagasse. Bagasse is the fibrous by-product generated after the milling of sugar cane in the production of raw sugar. The potential of sugar cane bagasse as a precursor in the manufacture of activated carbon is well recognized (Syna and Valix 2003; Valix et al. 2004; Zhang et al. 2005). Chemical treatment of bagasse has been shown to generate activated carbon with high surface area and fine pore structure (Valix et al. 2004). In this study, our aim was to investigate the effect of sulfur fixation on the surface chemistry of activated bagasse and its subsequent impact on the uptake of acid blue dye.

2 Experimental section

2.1 Preparation of the activated carbons

Bagasse was activated by physical activation. This involved a two step process: 1) carbonization of bagasse through the use of a dehydrating agent, sulfuric acid, followed by 2) gasification with carbon dioxide at 900 °C to develop the extended surface area and porous structure of chars. In the carbonization step, concentrated sulfuric acid was added to bagasse in an optimum ratio of 3:4 ratio (by weight) (Valix et al. 2004, 2006; Zhang et al. 2005). The blend was packed into a Pyrex reactor and heated to 160 °C for two hours with air. Air was metered into the reactor at the rate of 120 dm^3/s. The resulting carbon was cooled and washed with water until acid free and then dried at 110 °C. Gasification of the carbonized chars was conducted using various concentrations of carbon dioxide including 10, 50 and 100% (v/v) at a fixed temperature of 900 °C.

2.2 Physical and chemical characterization of the activated carbons

Textural characteristics of the carbon were determined by N_2 adsorption at 77 K in a Quantachrome Autosorb 1-CLP. The carbon pH values were determined according to ASTM test D3838-80 (ASTMA 1996). Chemical characterization also included sulfur analyses of activated bagasse which were conducted using an Elementar Vario EL III CHNOS elemental analyzer. The surface functional groups of the activated carbon were examined by Fourier transform infrared spectroscopy (Bruker IFS66v). To obtain the observable adsorption spectra, the activated carbon was ground to very fine powder and then dried at 120 °C for at least 24 hours. The dilution and homogenization of the fine carbon sample to approximately 0.1 wt% with KBr (spectroscopic grade) were carried out with additional grinding. Discs (12.7 mm I.D. and approximately 1 mm in thickness) were prepared using hydraulic press at 10 tons pressing time of 0.5 min. The spectra were measured and recorded (2500–500 cm^{-1}) with a resolution of 2 cm^{-1}.

2.3 Dye adsorption

The adsorbate used in this experiment is Acid Blue 80, AB80, (C.I. 61585, F.W. 678.68 mol/g) from CIBA. The molecular dimension was estimated to be 13.32 × 12.36 × 2.12 Å using the ChemSketch software (ACD/Labs) and its molecular structure is shown in Fig. 1.

Adsorption was carried out at room temperature using a fixed loading ratio of 10 mg of carbon in 10 ml of dye solution. Various dye concentrations from 20 to 1000 ppm were shaken with the carbon for a period of three weeks. Residual dye concentrations were measured using a UV/VIS spectrophotometer (Varian Cary 1E) at λ_{max} of 626 nm. All experiments were carried out in duplicate. The amount of dye adsorbed, Q_e (mg/g) was determined as follows:

$$Q_e = (C_o - C_e)V/W \tag{1}$$

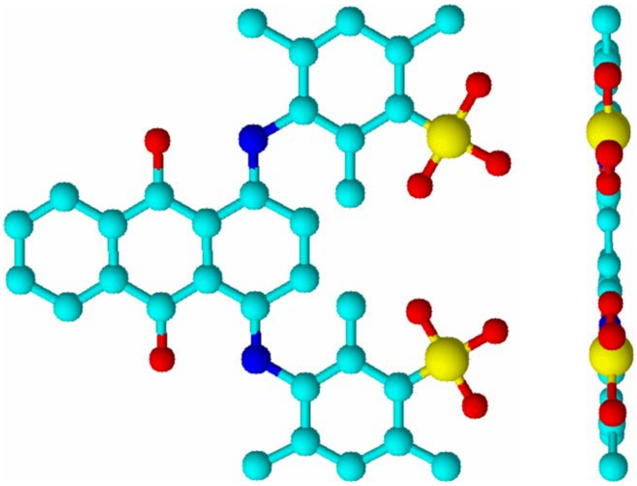

Fig. 1 Molecular structure of Acid Blue 80 (AB80)

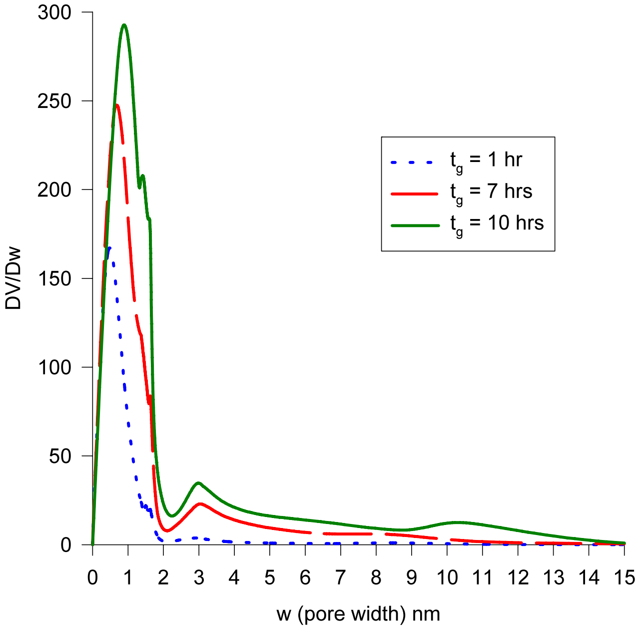

Fig. 2 Pore size distribution of carbons activated with 100% P_{CO_2} at 900 °C

where C_o and C_e are the initial and equilibrium liquid phase concentrations of the dye solution (mg/dm^3), respectively, V is the volume of the dye solution (dm^3), and W is the mass of dry carbon sample used (g).

3 Results and discussion

3.1 Textural properties of physically activated carbons from bagasse

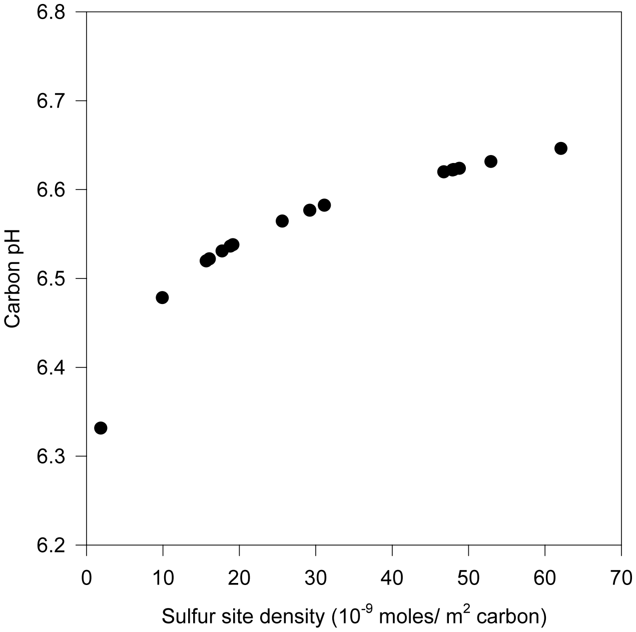

Fig. 3 The effect of sulfur site density on carbon surface pH

The total surface areas of the activated carbon from bagasse were calculated from the nitrogen adsorption by the BET equation (Brunauer et al. 1938). The molecular area of the nitrogen adsorbate was taken as 16.2 Å^2. The median pore width (W) of the micropores (pore size $<$ 2.0 nm) were estimated by applying the Horvath-Kawazoe (HK) method (Horvath and Kawazoe 1983) which assumes slit pore shapes. As shown in Fig. 2, the carbons generated from bagasse by the physical technique used in this study generated predominantly microporous structures with a slight contribution to porosity within the meso-macropore area. The textural properties of these physically activated carbons are summarized in Table 1.

The relative advantage of low sulfur chemical fixation with sulfuric acid is that it does not appear to interfere with the textural development of the carbon as often observed with immobilization of sulfur by pyrolytic methods. Table 1 shows the textural development of the carbons, reflected by the total surface areas, pore size and pore volumes are relatively unaffected by increasing sulfur contents. The lowering of the surface area observed in CC-6 carbon appears to be associated with pore collapse observed with extensive burnoff of the carbon rather than sulfur fouling.

3.2 Effect of sulfur fixation on the surface chemistry of the carbon

3.2.1 Carbon pH

Zhang et al. (2005) has recently reported that sulfur and nitrogen contribute to the alkalinity of carbons, whereas oxygen and hydrogen contribute to the acidity of the carbon surface. Figure 3 shows the effect of sulfur site density on the

Table 1 Physical properties of physically activated bagasse

Carbon adsorbent	P_{CO_2}%	Period of activation (hours)	BET TSA (m^2/g)	W (Å)	Pore volume (cm^3/g)	S (wt%)
CA-1	10	1	482	5.46	0.254	0.003
CA-2	10	3	546	4.87	0.289	0.033
CA-3	10	5	565	4.82	0.294	0.087
CA-4	10	7	661	5.12	0.351	0.066
CA-5	10	10	890	5.56	0.489	0.046
CA-6	10	15	992	6.66	0.579	0.093
CB-1	50	1	516	4.95	0.261	0.026
CB-2	50	5	681	4.92	0.349	0.056
CB-3	50	7	894	5.13	0.481	0.055
CB-4	50	10	876	6.5	0.489	0.137
CB-5	50	15	1161	10.7	0.749	0.174
CC-1	100	1	614	4.9	0.31	0.035
CC-2	100	3	737	4.54	0.387	0.125
CC-3	100	5	860	6	0.464	0.132
CC-4	100	7	1146	8.32	0.666	0.228
CC-5	100	10	1433	11.6	0.912	0.229
CC-6	100	15	1165	10.7	0.698	0.218

carbon pH. These carbon pHs were corrected for the effect of the average values of N (270×10^{-9} moles/m^2 carbon), O (10×10^{-9} moles/m^2 carbon), and H (20×10^{-9} moles/m^2 carbon) site densities of the carbons using the correlation proposed by Zhang et al. (2005). As shown, increasing sulfur site density contributes to the alkalinity of the carbon surface.

The nature of carbon basicity that arises as a result of the sulfur immobilization on the carbon surface is thought to arise from the Lewis base property of sulfur groups. Sulfur groups are electron pair donors that provide sites of π electron rich regions within the basal planes of the graphitic microcrystals that act as basic sites. There are several carbon-sulfur compounds that can exist on the carbon surface including sulfide, thiophenol, disulfide, thioquinone, sulfoxide and thioactone (Bandosz and Ania 2006). In solution, for example, the sulfur immobilized surface (CS_π) interacts with protons to produce an alkaline suspension and positively charged surface:

$$CS_\pi + H_2O \rightarrow CS_\pi - H^+ + OH^- \tag{2}$$

3.2.2 *FTIR*

Figure 4 shows the FTIR spectra of carbon activated from bagasse with 100% P_{CO_2} at 900 °C for 15 hours. The peaks from 1390 to 462 cm^{-1} represent the C=S, S=O and S=S stretching vibrations due to sulfur compound bonded to the activated carbons. The most significant absorbance peak is at 1087 cm^{-1}. This is characteristic of the S–O–C stretching. The presence of these functionalities are consistent with the reported functionalities of fixed sulfur in activated carbons prepared from sulfur and sulfur based compounds (Yamaki et al. 2002). The persistence of these sulfur groups even after 15 hours of activation reflects the general stability of these sulfur groups. The peaks at 3434 and 3258 cm^{-1} are characteristics of O–H stretching of hydroxyl and N–H stretching of amide oxygen complexes. The presence of these oxygen complexes may add a polar nature to activated carbons, for example hydrophilicity and acidity to the carbon surface.

3.3 Effect of sulfur functional groups on the acid blue dye adsorption capacity

The effect of introducing various quantities of sulfur on the equilibrium acid blue dye adsorption capacities are shown in Fig. 5. Adsorption capacities in Fig. 5 were normalized by the total surface areas of the carbon. As shown in Fig. 5, the relative effect of sulfur content of 0.003% to 0.132% on the dye adsorption capacities are negligible. However, sulfur concentrations above 0.218% appear to significantly enhance the dye adsorption capacity, comparing with adsorption capacity of 112.3 mg/g carbon with a commercially available activated carbon, F400 (Choy et al. 2000). This suggested the enhanced adsorption capacities are related to the more active surface chemistry associated with the higher sulfur functional groups. As sulfur groups impart a positively charged surface, the adsorption of the negatively

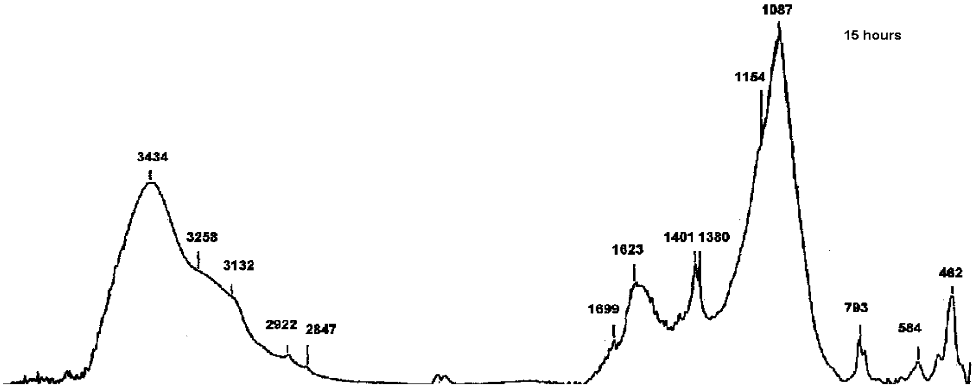

Fig. 4 FTIR spectra of carbon activated after 15 hours with 100% P_{CO_2} at 900 °C

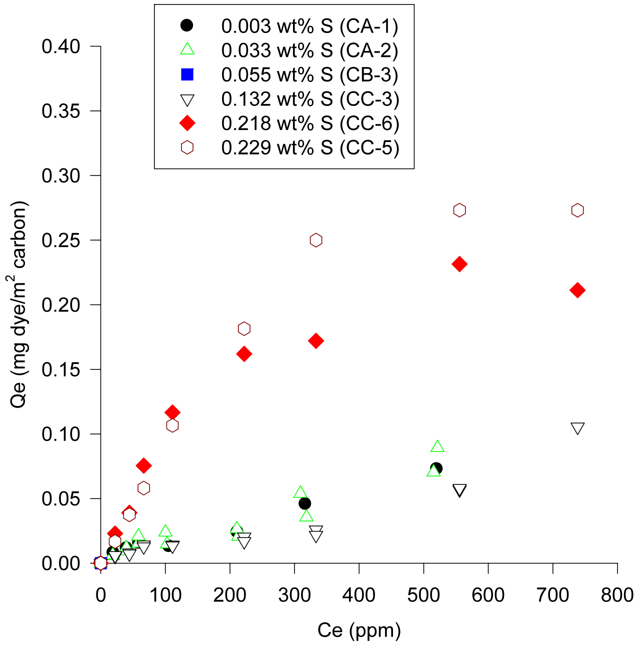

Fig. 5 The effect of sulfur concentration on the normalized equilibrium acid blue dye adsorption capacity of activated bagasse

charged acid dye is promoted onto the basic surface, in the case of $CS_\pi - H^+$:

$$CS_\pi - H^+ + Dye^- \rightarrow CS_\pi - H^+ - - - Dye^- \qquad (3)$$

3.4 Effect of sulfur functional groups on acid blue dye adsorption mechanism

In order to optimize the design of an adsorption system to remove dye, it is important to establish the most appropriate correlations for the equilibrium data for each system. Two isotherm equations have been tested in the present study, Langmuir (1918) and Freundlich (1906) models. The applicability of the isotherm equations is compared by judging the correlation coefficients, R^2.

The Langmuir equation is the most widely used two parameter equation commonly expressed as:

$$\frac{C_e}{Q_e} = \frac{1}{K_L Q_m} + \frac{1}{Q_m} C_e \qquad (4)$$

K_L is a direct measure for the intensity of the adsorption process (dm^3/mg) and Q_m is the constant related to the area occupied by a monolayer of adsorbate, reflecting the adsorption capacity (mg/g). From a plot of C_e/Q_e vs C_e, Q_m and K_L can be determined from its slope and intercept.

The Freundlich isotherm (Freundlich 1906) is an empirical equation commonly expressed as:

$$Q_e = K_F C_e^{1/n} \qquad (5)$$

in which it is characterized by the heterogeneity factor $1/n$ and K_F is the Freundlich constant (dm^3/mg$^{1-1/n}$/g). When $n = 1/n$, the Freundlich equation reduces to Henry's Law. This isotherm is another form of the Langmuir approach for adsorption on an "amorphous" surface. The amount adsorbed material is the summation of adsorption on all sites. The Freundlich isotherm is derived by assuming an exponential decay energy distribution function inserted in to the Langmuir equation. It describes reversible adsorption and is not restricted to the formation of the monolayer. A summary of the fitted adsorption model parameters is shown in Table 2.

The acid blue dye adsorption was found to fit the Freundlich model in general. The effect of sulfur functional groups on the carbon adsorption behavior was further examined by correlating the Freundlich $1/n$ and K_F constants with the sulfur content of the carbon in Figs. 6 and 7, respectively. Figure 6 suggests that lower sulfur content promotes cooperative adsorption. Examination of Table 1 shows carbons with lower sulfur content also have narrower mean pore diameters. As such the effect of sulfur and textural properties of the carbon on the mechanism of adsorption cannot be decoupled. The general fit of the acid blue dye adsorption towards Freundlich model for the activated bagasse in this study imply these carbons promote cooperative adsorption.

Table 2 Fitted acid blue dye adsorption model parameters

Carbon	Langmuir model			Freundlich model		
adsorbent	Q_m (mg/g)	K_L 10^3 (L/mg)	R^2	$1/n$	K_F mg/g(L/mg)$^{1/n}$	R^2
CA-1	59.5	1.85	0.34	0.87	0.13	0.94
CA-2	16.9	7.9	0.33	0.67	0.23	0.91
CA-3	75.8	1.9	0.23	0.56	1.13	0.89
CA-4	43.9	4.7	0.58	0.46	1.69	0.85
CA-5	78.1	8.4	0.89	0.4	5.18	0.93
CA-6	96.2	8.5	0.94	0.34	11.31	0.86
CB-1	46.1	1.9	0.5	0.75	0.21	0.93
CB-2	68.5	1.8	0.26	0.62	0.62	0.91
CB-3	90.1	1.4	0.13	0.845	0.232	0.93
CB-4	217.4	1.2	0.2	0.78	0.68	0.95
CB-5	80	22.1	0.94	0.29	22.87	0.86
CB-6	333.3	22	0.99	0.32	48.76	1
CC-1	333.3	0.27	0.03	0.98	0.135	0.96
CC-2	59.9	2.8	0.46	0.6	0.81	0.9
CC-3	75.2	8.1	0.68	0.31	7.94	0.8
CC-4	169.5	62.5	0.99	0.23	50.2	0.91
CC-5	384.6	329.1	1	0.14	187.54	1
CC-6	277.8	455.7	0.97	0.28	44.72	0.91

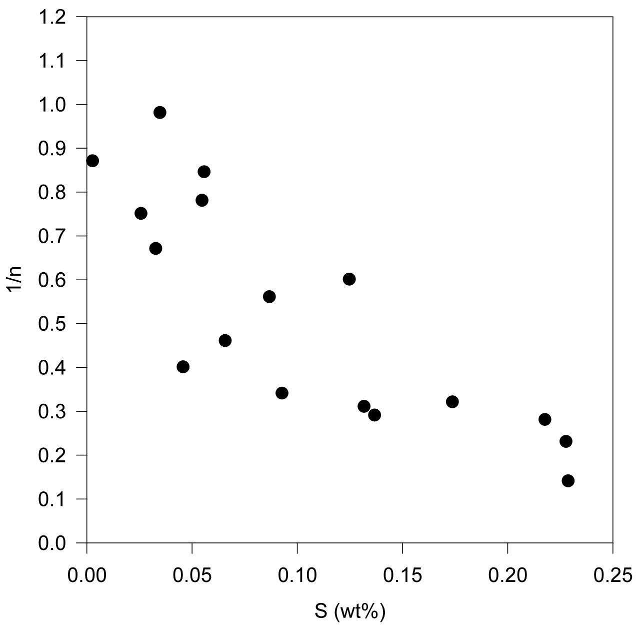

Fig. 6 Effect of sulfur on the acid blue dye adsorption intensity on activated bagasse

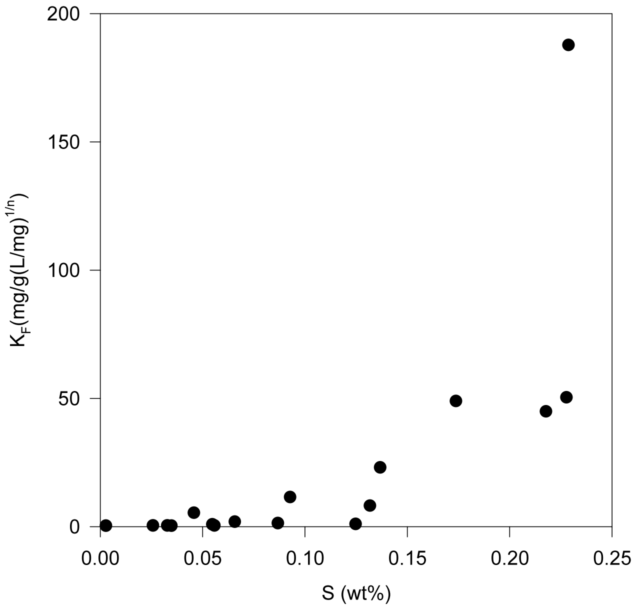

Fig. 7 Effect of sulfur on the acid blue dye distribution coefficient on activated bagasse

Figure 7 shows sulfur contents above 0.12% appear to significantly enhance the adsorption bonding of the acid blue dye on the carbon surface.

4 Conclusions

This study has demonstrated that sulfur based functional groups can be chemically fixed using sulfuric acid treatment of biomass prior to gasification. The introduction of sulfur groups by this method was able to impart improvements on the surface functional groups without interfering with the textural development of the carbons as often observed with pyrolytic introduction of high concentrations of sulfur. Functional groups including C=S, S=O and S=S and S–O–C were observed on the carbon surface. These groups once introduced on the carbon surface exhibited thermal stability even after gasification with 100% CO_2 at 900 °C for 15 hours. In general the carbon also contained oxygen complexes that would promote acidic sites. In general sulfur contents from 0.003 to 0.229 wt% appear to impart alkalinity or positively charged carbon surface. The effect of sulfur contents above 0.2% appears to significantly enhance adsorption capacities of the carbon. Acid dye capacities increased by as much as 700% with the introduction of 0.229% S on activated bagasse over carbon with no sulfur.

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