

Role of heteroatoms in activated carbon for removal of hexavalent chromium from wastewaters

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Abstract

Heteroatoms are elements including sulfur, nitrogen, oxygen and hydrogen which are found on the surface of activated carbons. This study investigated the surface modification arising from heteroatoms bonding to carbon aromatic rings within the activated carbon and their corresponding influence on the chromium adsorption process. Activated carbons were prepared from bagasse by physical. Chromium removal capacities of these activated carbons by adsorption and reduction were determined. Models which related the chromium adsorption and reduction capacities of activated carbons to carbon acidity and heteroatom site concentrations were established using multi-variable linear regression method. It was found the individual heteroatoms contributed separately to the basicity of the carbon which in turn determined the mechanism by which chromium was removed from solution. The surface areas of the carbons were also observed to influence the adsorption and reduction of chromium. These understandings provide the fundamental method of optimising chromium removal through suitable control of carbon surface chemistry and textural properties.

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1. Introduction

Activated carbon has been prepared from various low cost agricultural by-products such as maize cob, wood, plum stone, peach stone and rice hull [1–3]. Bagasse from the sugar milling process, is of particular interest because it is a renewable resource and because of its availability, quantity and low cost. Approximately 11 million tonnes of bagasse or greater and equivalent quantity of cane field trash are produced in Australia annually. A fraction of this fibre is used to co-generate both steam and power for the sugar mills. The current practice is to burn these fibres inefficiently in sugar mill boilers to reduce residual quantities of bagasse and to avoid the cost and potential environmental and safety hazards associated with its storage. Despite this practice, in most seasons, large quantities of bagasse are produced. The production of activated carbon from bagasse offers a huge opportunity to overcome these problems and to generate additional income for sugar mills.

Many separation techniques have been proposed for the removal of heavy metal effluents from wastewaters including co-precipitation, coagulation, ion exchange, membrane filtration and adsorption [4–9] and bio-sorption [10,11]. Although adsorbents are used abundantly throughout the water and wastewater treatment industries, carbon adsorption remains an expensive process. This is associated with the high cost of producing activated carbons [12]. Optimising the efficiency and the selective adsorption capacity of activated carbon would require a greater understanding of the surface metal adsorption process.

This study investigated the contribution of heteroatoms including sulfur, nitrogen, oxygen and hydrogen, to the surface acidity of activated carbon and their corresponding influence in the removal of chromium. Adsorption of heavy metals has been found to be influenced by surface chemistry of carbon inferred from its acidity or carbon pH. Basic and acidic carbons are generally recognized as having positive and negative surface charges, respectively [13,14] which are postulated to provide the selectivity to attract anionic and cationic metal groups to the carbon surface. The acidity can be measured by acid/base titration [15] to provide the pH required to give a zero net charge, mass titration [16] or by measurement of the corresponding pH imparted

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Nomenclature

a	exponent for sulfur in the reduction model (model 1)
adjusted- r^2	coefficient of determination adjusted for a number (p) of variables
b	exponent parameter for nitrogen in the reduction model (model 1)
c	exponent parameter for hydrogen in the reduction model (model 1)
Cr_{ads}	adsorbed chromium (Cr(VI) + Cr(III) mg/g carbon)
Cr_e	chromium removal efficiency from solution (Cr(removed by adsorption)/Cr in the feed solution) (wt.%)
Cr_{red}	Cr(VI) reduced to Cr(III) (Cr(III) mg/g carbon)
d	exponent parameter for oxygen in the reduction model (model 1)
F	F -statistics
[H]	hydrogen site concentration (mmol/g carbon)
k	number of predictor variables in the reduced model
$k_{Cr(III)}$	constant term in models 3 and 4
$k_{Cr(VI)}$	constant term in model 2
k_p	constant term in model 1
MSE	mean error ((mg Cr(adsorbed)/g carbon) ²)
n	number of carbon tested
[N]	nitrogen site concentration (mmol/g carbon)
[O]	oxygen site concentration (mmol/g carbon)
p	number of predictor variables in the model
p -values	probability
P_{CO_2}	partial pressure of carbon dioxide (v/v, %)
q_{mean}	mean adsorption capacity (mg Cr(adsorbed)/g carbon)
$q_{measured}$	experimental adsorption capacity (mg Cr(adsorbed)/g carbon)
$q_{predicted}$	predicted adsorption capacity (mg Cr(adsorbed)/g carbon)
r^2	coefficient of determination
$R(M_1/M_2)$	reduced error sum of the squares ((mg Cr(adsorbed)/g carbon) ²)
s_e	mean square error (mg Cr(adsorbed)/g carbon)
[S]	sulfur site concentration (mmol/g carbon)
SSE	sum of squared errors ((mg Cr(adsorbed)/g carbon) ²)
SSR	sum of squares for regression ((mg Cr(adsorbed)/g carbon) ²)
SST	sum of squared total ((mg Cr(adsorbed)/g carbon) ²)
TSA	total surface area (m ² /g)
<i>Greek letters</i>	
α	exponent for sulfur in the reduction model (model 2)
β	exponent parameter for nitrogen in the reduction model (model 2)

γ	exponent parameter for hydrogen in the reduction model (model 2)
δ	exponent parameter for oxygen in the reduction model (model 2)
η	exponent parameter for sulfur in the reduction model (models 3 and 4)
κ	exponent parameter for hydrogen in the reduction model (models 3 and 4)
μ	exponent parameter for nitrogen in the reduction model (models 3 and 4)
ρ	exponent parameter for oxygen in the reduction model (model 3)

by the carbon adsorbent in the bulk solution [17]. Boehm [18] suggested that the surface acidity is a contribution of various acidic and basic functional groups which can be titrated with HCl, NaOH, NaHCO₃ and Na₂CO₃. It has been suggested that a similar relationship exists between elemental or heteroatom sites and carbon acidity. Hydrogen, oxygen, sulfur and nitrogen are elements found on the surfaces of activated carbons. Their presence is found to affect the surface acidity and adsorption properties of activated carbon [19–22]. However, with the exception of oxygen, little has been done to elucidate the individual and or complementary effects of nitrogen, hydrogen and sulfur heteroatoms on the surface of activated carbons.

Heteroatoms provide charged groups in the carbon structure. These groups can reside within the carbon layers forming heterocyclic rings, or bonded to edges and corners of the aromatic rings or carbon defect positions. Carbon atoms retaining these heteroatom groups have unsaturated valencies. Since these sites are the main adsorbing sites, the presence of heteroatoms or molecular species is expected to modify the surface characteristics and surface behaviour of these carbons [20]. Surface modification of bagasse, in particular sulfur fixation, has been shown to promote the adsorption of heavy metals [23].

The role of heteroatom surface sites in the removal of chromium was investigated in this study. Chromium is usually found in industrial wastewaters with the most common sources coming from electroplating, leather tanning and textile industries. Chromium, in wastewater can exist both as Cr(III) and Cr(VI). However, in potable waters, Cr(VI) appears as the most stable species due to the aerobic conditions in this environment. The trivalent form is not considered toxic. On the other hand, the detrimental effects of hexavalent chromium to biological systems and the environment have been well documented [24]. Exposure to Cr(VI) can have damaging effects on the human physiological, neurological and biological systems when tolerance levels are exceeded. Several procedures have been proposed to remove hexavalent chromium from industrial wastewaters [25,26]. These include chemical reduction and precipitation, ion exchange, evaporation and concentration, electrolysis and electroplating, ion flotation, activated sludge process and carbon adsorption. Adsorption of heavy metals onto activated carbon is

found to be the most effective in particular for the removal of low concentrations of metal ions.

The removal of Cr(VI) from wastewater by adsorption onto carbon surfaces can be accompanied by the reduction of Cr(VI) to Cr(III) and possible further precipitation to Cr(OH)₃ under neutral or slightly alkaline conditions. Previous studies suggest that efficient adsorption require that chromium be maintained as Cr(VI) since Cr(III) adsorption onto activated carbon is met with difficulty because of its high coordination with water [27]. The precipitation to Cr(OH)₃, should this occur within the carbon, would cause severe problems in regenerating the carbon because of the low solubility of this precipitate. The removal of Cr(VI) by activated carbon is a complex process which requires a thorough understanding of the speciation of chromium in solution under various conditions and the role of the carbon properties in the removal of these species.

In this study, activated carbons from bagasse were used as adsorbents for the removal of chromium from wastewater. The specific interest in this investigation was to elucidate the role of the heteroatoms (S, N, H and O) within the carbon in determining the surface acidity of activated carbon and the corresponding effect on the chromium removal by both adsorption and reduction. Since adsorption is a surface effect, the role of the carbon surface areas was also considered.

2. Experimental

2.1. Preparation of the activated carbons by physical activation

Activation of bagasse in this study 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 a 3:4 ratio (by weight). The blend was packed into a Pyrex reactor and heated to 160 °C for 2 h with air. Air was metered into the reactor at the rate of 2 l/min. The carbon was cooled and washed with water until acid free and dried at 110 °C. Detailed description of the gasification unit and procedures used in this study have been reported [28–30]. Gasification of the carbonized chars was conducted using various concentrations of carbon dioxide including 10, 50 and 100% (v/v). The gasification conditions used in the preparation of the adsorbents are reported in Table 1.

2.2. Physical and chemical characterization of the activated carbons

The ash and pH of the activated carbons were determined according to ASTM tests D2866-94 and D3838-80, respectively [17]. The pH test involved boiling 10 g of carbon in 100 ml of water for 15 min. The solution was filtered and the pH of the filtrate measured at 50 °C. The ash test involved taking pre-dried carbon sample and ashing it in a muffle furnace at 650 °C for 4 h. The ash content was calculated from the residue left after the sample was burnt in the fur-

Table 1
Gasification conditions of physically activated carbon from bagasse

Carbon adsorbent	P _{CO2} (v/v, %)	Period of activation (h)
CA-1	10	1
CA-2	10	3
CA-3	10	5
CA-4	10	7
CA-5	10	10
CB-1	50	1
CB-2	50	3
CB-3	50	5
CB-4	50	7
CB-5	50	10
CB-6	100	15
CC-1	100	1
CC-2	100	3
CC-3	100	5
CC-4	100	7
CC-5	100	10
CC-6	100	15

nace. The test was repeated until constant ash content was obtained.

The total surface area was determined by N₂ adsorption at 77 K in Quantachrome Autosorb 1-CLP. Total surface areas were calculated from the nitrogen adsorption by the BET equation [31]. The molecular area of the nitrogen adsorbate was taken as 16.2 Å². The carbon, hydrogen, nitrogen and sulfur analyses of activated bagasse were conducted using Elementar vario EL III CHNOS elemental analyser. The oxygen content of the carbon was estimated by difference between C, H, N, S and the ash content of the carbon.

2.3. Chromium adsorption

A 5 mg/l synthetic chromium solution was prepared by dissolving potassium dichromate in distilled water and adjusting the pH to 2.0. The solution was prepared from analytical grade reagents. The choice of these two conditions is dictated by the surface charge of the carbon and chromium speciation that has been previously shown to result in optimum chromium adsorption from solution [32]. The solution pH of 2, chosen for these tests, ensured adsorption was conducted at pH below the isoelectric point of the carbon used. Below the isoelectric point, the carbon will have a positive charge and would therefore promote the adsorption of the negatively charged chromium species. Typical industrial chromium effluents are 5–220 mg/l [33,34]. In this study, the lower concentration of 5 ppm was chosen for several reasons: (i) most metal removal techniques including co-precipitation, membrane techniques, solvent extraction are challenged by the removal of lower concentrations of metal from solution. Adsorption by activated carbon may present certain advantages in mopping up these lower concentrations of metals; and (ii) lower chromium concentration will maintain the dominant presence of the smaller HCrO₄⁻ species rather than the dimerized Cr₂O₇²⁻ anion species [35]. This should reduce diffusional resistance of the chromium species allowing its greater access into the carbon structure.

Table 2
Physical and chemical characteristics of physically activated bagasse and their corresponding chromium removal capacities

Carbon	[S] ^a	[N] ^b	[H] ^c	[O] ^d	Ash (wt.%)	Carbon pH	TSA (m ² /g)	Cr _{ads} ^e	Cr _e ^f	Cr _{red} ^g
CA-1	0.001	0.13	11.78	6.05	21.6	6.1	482	3.4	6.8	0.5
CA-2	0.010	0.12	12.29	6.21	22.9	6.3	546	3.6	7.2	0.9
CA-3	0.027	0.11	13.78	3.22	28.8	6.1	565	4.9	9.8	0.9
CA-4	0.021	0.12	5.00	1.25	32.9	6.4	661	7.7	15.4	2.9
CA-5	0.014	0.12	5.00	15.00	34.2	6.4	890	7.2	14.4	3.5
CB-1	0.008	0.13	17.00	9.38	19.6	6.1	992	4	8.0	5.2
CB-2	0.018	0.12	14.53	6.76	27.7	6.2	516	3.9	7.8	1.2
CB-3	0.017	0.10	14.08	9.69	32.3	6	681	4	8.0	1.3
CB-4	0.043	0.16	16.79	1.76	40	6.5	894	5.2	10.4	0.6
CB-5	0.054	0.15	10.75	5.98	46.1	6.6	876	5.7	11.4	2.1
CC-1	0.011	0.12	12.00	6.00	46.1	6.4	1161	4.5	9.0	5.1
CC-2	0.039	0.13	16.03	8.50	28.7	6.5	614	6.4	12.8	1.2
CC-3	0.041	0.18	16.00	1.88	34.8	6.8	737	6.8	13.6	1.9
CC-4	0.071	0.18	15.64	0.82	44.3	7.1	860	7.3	14.6	3.9
CC-5	0.072	0.14	3.39	2.75	61.1	7.4	1146	11.4	22.8	6.9
CC-6	0.068	0.17	7.74	8.80	46.7	7.4	1433	10.1	20.2	9.4

^a [S]: sulfur site density (mmol/g carbon).

^b [N]: nitrogen site density (mmol/g carbon).

^c [H]: hydrogen site density (mmol/g carbon).

^d [O]: oxygen site density (mmol/g carbon).

^e Cr_{ads} is the adsorbed chromium (Cr(VI) + Cr(III) mg/g carbon).

^f Cr_e is the chromium removal efficiency from solution (Cr(removed by adsorption)/Cr in the feed solution) (wt.%).

^g Cr_{red} is Cr(VI) reduced to Cr(III) (Cr(III) mg/g carbon).

Adsorption tests were carried out by equilibrating 50 mg of activated carbon with 500 ml of chromium solution at room temperature. The pH of the solutions was adjusted further with 0.1 M HCl or NaOH to pH 2.0 after the addition of the carbon into the Cr(VI) solution. Samples were taken at various intervals of time, filtered and analysed. Total chromium concentrations (Cr(VI) and Cr(III)) in solution were determined with a Varian SpectraAA-10 atomic absorption spectrophotometer. Hexavalent chromium concentrations were determined by colorimetric analysis using 1,5-diphenylcarbazide according to the standard methods [36]. The absorbance was read on a UV/vis spectrometer (UNICAM 8625) at a wavelength of 540 nm. Trivalent chromium in solution was measured by subtracting the hexavalent chromium concentration from the total measured using the atomic absorption spectrophotometer.

3. Results and discussion

3.1. Physical, chemical properties and chromium removal capacities of activated carbons

The textural and chemical properties resulting from activation of bagasse are important in the adsorption properties of the generated activated carbons. Table 2 shows the characteristics of physically activated bagasse including heteroatom site densities, ash content and carbon pH and the corresponding chromium adsorption and reduction capacities. Chromium adsorption data have been expressed both as chromium adsorbed normalized by the weight of carbon (chromium adsorbed (mg)/g carbon) and as chromium removal efficiency (chromium removed by adsorption/chromium in the feed solution (wt.%)). The heteroatom

site densities of activated bagasse, [S], [N], [O] and [H] were expressed in terms of the number of moles of oxygen, hydrogen, nitrogen and sulfur per unit dry weight of carbon. In this study, the chromium adsorbed was assumed to be the sum of Cr(VI) and Cr(III) complexes. Adsorption and reduction capacities were estimated based on dry weights of carbon.

Table 2 shows most of the physically activated carbon contained sulfur sites between 0.01 and 0.07 mmol/g. This is attributed to the carbonization of bagasse with sulfuric acid as part of the physical activation method in preparing activated carbon. It is apparent that the sulfur from this technique is retained in the activated carbon even after gasification with carbon dioxide at 900 °C. This technique can thus be used to fix low concentrations of sulfur onto activated carbon. The carbon pHs are from 6 to 7.4 which indicate weakly acidic surfaces and generally neutral surfaces were generated by the activation techniques used in this investigation.

3.2. Contribution of heteroatoms to carbon pH in physically activated carbons

Table 2 shows that direct correlation of the carbon pH to individual heteroatom site concentrations, the oxygen [O], hydrogen [H], nitrogen [N] and sulfur [S], is complicated by the concurrent development of these parameters with the extent of activation. To decouple the contributions of each heteroatom, the following correlation of the carbon surface pH and heteroatom concentrations was proposed using the properties of physically activated carbons generated in this study:

$$\text{Model 1: carbon pH} = k_p[S]^a[N]^b[H]^c[O]^d \quad (1)$$

Table 3
Parameters of pH model according to Eq. (1)

Parameters	Values
k_p	12.15
a	0.025
b	0.17
c	-0.07
d	-0.0028

where k_p is a constant and [S], [N], [H] and [O] are the sulfur, nitrogen, hydrogen and oxygen site concentrations (mmol/g carbon).

The parameters of model 1 were determined by multi-linear regression. The parameters are shown in Table 3.

3.3. Error analysis of the carbon pH models

Error functions were defined to determine the values and significance of each parameter in model 1 and to establish the fit of the model to the experimental data. The sum of the squared variation of the experimental adsorption capacities (q_{measured}) and predicted data ($q_{\text{predicted}}$) to the mean experimental adsorption capacities ($q_{\text{measured, mean}}$) and the sum of the squared residual between experimental and predicted adsorption values form the basis of the error analysis of the fitted model in this study. The sum of squared total (SST), sum of squares for regression (SSR) and sum of squared errors (SSE) were computed from the (n) number of carbon tested as follows [37]:

$$\text{SST} = \sum_{i=1}^n (q_{\text{measured}} - q_{\text{mean}})^2 \quad (2)$$

$$\text{SSR} = \sum_{i=1}^n (q_{\text{predicted}} - q_{\text{mean}})^2 \quad (3)$$

$$\text{SSE} = \sum_{i=1}^n (q_{\text{measured}} - q_{\text{predicted}})^2 \quad (4)$$

The variance of the random errors between the fitted model and the observed data can be measured from the value of SSE averaged with the degree of freedom according to the following equation [37]:

$$s_e^2 = \text{MSE} = \frac{\text{SSE}}{\text{degree of freedom}} \quad (5)$$

s_e is also referred to as the mean square error.

The parameters of model 1 were determined using the solver “add-in” function of Microsoft Excel spreadsheet program by minimizing SSE. These parameters are shown in Table 4.

3.4. Parameter significance tests

The significance of the independent variable used in model 1 was established using a partial F -test. The error sum of the squares of the full model is SSE_1 and that of the reduced model

Table 4
Statistical significance of model 1 parameters ($n = 19$; $p = 4$)

Parameters	Degree of freedom	SSE	$R(M_1/M_2)$	MSE	F	p -Value
Full	14	0.62		0.04429		
S	1	1.608	0.99	0.99	22.3	0
N	1	1.7	1.08	1.08	24.4	0
H	1	1.23	0.61	0.61	13.8	0.002
O	1	0.8	0.18	0.18	4.1	0.025
Constant, k_p	1	27.5	26.88	26.88	607	0

containing k predictors is SSE_2 . The resulting from the fit of the additional terms in the full model was defined as [38]:

$$R \left(\frac{M_1}{M_2} \right) = \text{SSE}_2 - \text{SSE}_1 \quad (6)$$

The F -statistics for determining the statistical significance of the chosen subset of predictor variables is

$$F = \frac{\frac{R(M_1/M_2)}{p-k}}{\frac{\text{SSE}_1}{n-p-1}} = \frac{\text{MSR}(M_1/M_2)}{\text{MSE}} \quad (7)$$

The F -statistics was used to test the null hypothesis that the variances of the reduced and full model are equal. The significance of the observed F -test was measured from the p -value or significance probability. The p -values were estimated using the Statistica-6 package. If the p -value is less than the conventional 0.05 level, then the null hypothesis was rejected and the conclusion was that the two variances differed significantly and the variable removed in the reduced model was a statistically significant predictor in the adsorption of chromium on activated carbon. The F -tests of the parameters in model 1 are shown in Table 4. The parameters [S], [N], [H] and [O] of model 1 are shown to be statistically significant.

3.5. Goodness of fit of the carbon pH model

To further analyse the suitability of model 1, its fit to the experimental data was assessed. The overall success of the fit of the models can be determined from the extent by which the variation in the observed data is explained by the variation of the fitted model. This is measured from a single statistical parameter (r^2)—that is also referred to as coefficient of determination and was defined as follows [37]:

$$r^2 = \frac{\text{SSR}}{\text{SST}} \quad (8)$$

The values of r^2 vary from 0 (model does not account for the variability) to 1 (model accounts for all data variability). The correlation of the predicted and observed carbon pH is shown in Fig. 1. The fit of the pH model, judged from the regression correlation r^2 of 0.85, suggests a relatively good correlation. It should be emphasized however that the validity of the proposed model cannot be summarized by a single valued statistic. Furthermore the value of r^2 increases as the number of independent variables increases regardless of the significance or lack thereof of the

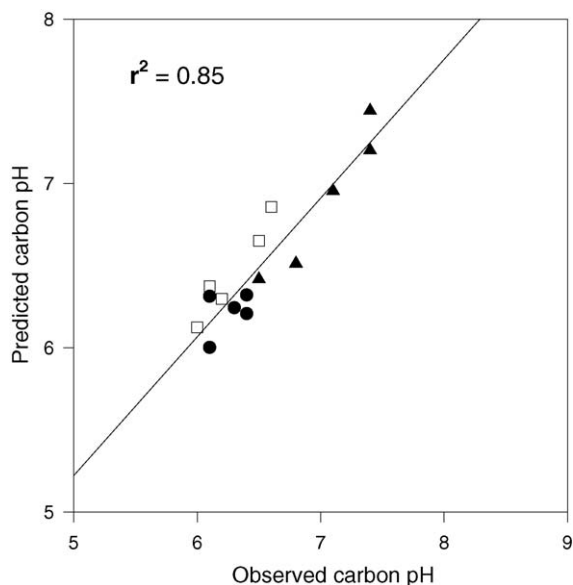


Fig. 1. Correlation of experimental and model fitted carbon pH: (●) 10% CO₂, 900 °C; (□) 50% CO₂, 900 °C; (▲) 100% CO₂, 900 °C.

added variable to the dependent variable. To overcome this misleading representation by r^2 , a variant called the adjusted- r^2 that adjusts for the number of variables (p) in the fitted model was also reported. The adjusted- r^2 will decrease if the added independent variable adds little to the ability of the model to explain the variation in the dependent variable; otherwise adjusted- r^2 will increase. The adjusted- r^2 was computed as [37]:

$$\text{adjusted } r^2 = 1 - \frac{(n-1)\text{SSE}}{(n-p-1)\text{SST}} \quad (9)$$

An alternative measure of the fit of the model is to determine the variance of the random errors through the mean square error. To correct for the bias of differing number of fitted dependent variable (p), the population number (n) was corrected to give a degree of freedom of $(n-p-1)$ according to the following equation [37]:

$$\text{MSE} = s_e^2 = \frac{\text{SSE}}{n-p-1} \quad (10)$$

The statistical measures of the fit of two proposed models are $r^2=0.84$, adjusted- $r^2=0.8$ and $s_e=0.21$. These statistical parameters suggest model 1 adequately describes the correlation between the heteroatom concentration in the carbon and their corresponding carbon pH.

Heteroatoms have been suggested to provide charged groups in the carbon structure. Bansal et al. [20] implied the presence of heteroatoms or molecular species will modify the surface characteristics and surface behaviour of carbon. Direct correlations between heteroatoms and the acidity of carbons have been sparse with the exception of oxygen groups [21,39–41]. The good fit achieved between the carbon pH and heteroatoms of physically activated carbons in Fig. 1 confirms the contribution of sulfur, nitrogen, hydrogen and oxygen atoms to the surface acidity of the carbon.

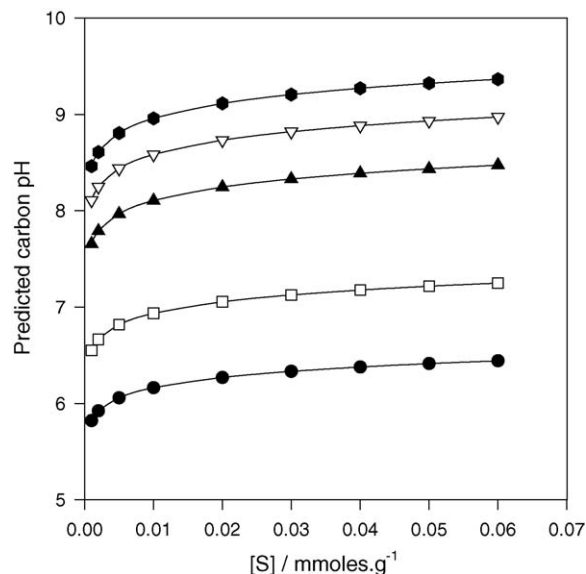


Fig. 2. Predicted carbon pH as a function of sulfur site density at various nitrogen site densities. Constant parameters—[H]=10 mmol/g and [O]=5 mmol/g: (●) [N]=0.1 mmol/g, (□) [N]=0.2 mmol/g, (▲) [N]=0.5 mmol/g, (▽) [N]=0.7 mmol/g (●), [N]=0.9 mmol/g.

The contributions of the heteroatom site concentration to the carbon pH are shown in Figs. 2 and 3. Model 1 was used to predict the carbon pH in these correlations. Both sulfur and nitrogen sites, as shown in Fig. 2, contribute to the basic surface of the carbon. Similar observations that report the effects of sulfur and nitrogen heteroatoms in surface acidity of carbons provide further confirmation of the role of sulfur and nitrogen in enhancing the basic properties of carbons. Otake and Jenk-

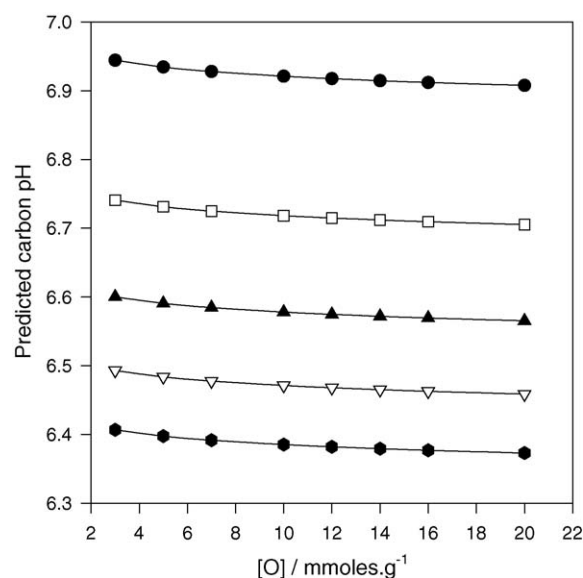


Fig. 3. Predicted carbon pH as a function of hydrogen site density at various oxygen site densities. Constant parameters—[N]=0.2 mmol/g and [S]=0.01 mmol/g: (●) [H]=0.1 mmol/g, (□) [H]=0.2 mmol/g, (▲) [H]=0.5 mmol/g, (▽) [H]=0.7 mmol/g, (●) [H]=0.9 mmol/g.

ins [39] have shown that carbons treated with HNO₃ showed a reduction in acidity for the same quantity of oxygen groups. This suggests the nitrogen groups, which remain in the carbon, impart a basic surface. Benaldi et al. [19] have shown similar effects of nitrogen compounds on the acidity of activated carbons.

The nature of carbon surface basicity, despite the demonstration of basic site properties through adsorption of acids, is still not well understood. There are essentially two schools of thought; one is based on the chromene model and the Lewis base concept [42]. The chromene groups are assumed to generate resonance stabilized carbonium ions by reduction/oxidation reaction in solutions. Lewis bases which are electron donors provide sites of π electron rich regions within the basal planes of the graphitic microcrystals that act as basic sites. Recently, the support for the Lewis base concept has been greater over the chromene model [21,42]. Sulfur and nitrogen compounds in particular oxides of sulfur and nitrogen are known to contain unpaired electrons. The observed effect of sulfur and nitrogen in the alkalinity of the carbon in this study also supports the Lewis base concept.

The correlation in Fig. 2 suggests the sulfur sites appear to have the greater influence only at the lower concentrations. Increasing the sulfur sites above 0.02 mmol/g has little influence on the carbon pH. This limiting influence was also observed with increasing nitrogen, hydrogen and oxygen sites. A similar observation has been made in the correlation between carbon pH and the surface oxygen level of BPL 900N₂ carbon [21]. Although the nature of this effect is not well understood, it is clear that only low concentrations of heteroatoms are effective in determining the surface chemistry of the carbon.

Fig. 3 shows the correlation of hydrogen and oxygen sites with carbon pH. Both hydrogen and oxygen are shown to contribute to the acidic property of the carbon. The effect of oxygen and hydrogen elements to the carbon surface has been reported and is consistent with the observations made in this study. Lopez-Ramon et al. [40] showed the pH zero point charge decreased rapidly as the oxygen content increased, which indicate a more acidic surface. He further concluded that oxygen complexes are predominantly of acidic character. Otake and Jenkins [39] have also shown the acidity of the carbon increased with the oxygen content. Barton et al. [21] demonstrated the carbon acidity increased with increasing O content while the basic site decreased. Toles et al. [22] suggested hydrogen atoms in carboxylic and hydroxyl groups are acidic in nature. Jankowska et al. [41] showed that oxygen and hydrogen treatment of carbon surfaces reduced the potential of electrolyte solution containing these pre-treated carbons. This is consistent with the formation of acidic surfaces.

The oxygen and hydrogen sites, of the carbons generated in this study, are an order of three and two magnitudes greater than sulfur and nitrogen sites respectively (see Figs. 2 and 3). The effects of nitrogen and sulfur sites to the carbon pH on the molar basis are significant in comparison to hydrogen and oxygen sites. This suggests that modification of the carbon pH to alkaline properties requires only a low concentration of fixed nitrogen and or sulfur groups.

Table 5

Parameters of the chromium adsorption (model 2) and chromium reduction (model 3) models

Cr(VI) adsorption (model 2)		Cr(VI) reduction to Cr(III) (model 3)	
Parameters	Values	Parameters	Values
$k_{Cr(VI)}$	106.7	$k_{Cr(III)}$	12481
α	0.173	η	0.37
β	0.63	μ	3.2
γ	-0.433	κ	-0.82
σ	-0.012	ρ	-0.003

3.6. Chromium removal

Heteroatoms such as oxygen, hydrogen, nitrogen and sulfur also have a strong influence on the mechanism of the adsorption process [20,42]. As previously suggested, this is associated with the influence of these elements to the surface charge of the carbon [20]. The contribution of the heteroatoms in activated bagasse for the removal of chromium ions from solution were also investigated in this study.

There are several physical and chemical interactions including the association of the inorganic constituents of the carbon that may contribute to the overall surface chemistry and thus metal adsorption onto the carbon. Such interactions are important but are also equally complex and difficult to accurately investigate because of the many possible phases of organic and carbon organic components that must first be identified, quantified and characterized. As such, in this study, only the specific effects of heteroatom to the surface chemistry and chromium removal were considered.

The removal of chromium by adsorption of Cr(VI) and reduction to Cr(III) were related to the heteroatom concentrations. The chromium removal was expressed in terms of chromium adsorbed per unit dry weight of carbon. Chromium reduction which was measured from the Cr(III), which remained in the solution after adsorption, was also expressed in terms of Cr reduced per unit dry weight of carbon. The simultaneous variation of the [O], [H], [N], and [S] site densities with activation makes direct correlation to chromium adsorption and reduction difficult. To decouple the individual effects of heteroatoms, the following correlation of chromium removal to heteroatom site densities were proposed:

$$\text{Model 2 : } Cr(VI) + Cr(III)_{\text{adsorbed}} = k_{Cr(VI)}[S]^{\alpha}[N]^{\beta}[H]^{\gamma}[O]^{\delta} \quad (11)$$

$$\text{Model 3 : } Cr(VI)_{\text{reduced to Cr(III)}} = k_{Cr(III)}[S]^{\eta}[N]^{\mu}[H]^{\kappa}[O]^{\rho} \quad (12)$$

where $k_{Cr(VI)}$ and $k_{Cr(III)}$ are constant terms in models 2 and 3, respectively. The parameters of models 2 and 3 were obtained through multi linear regression and the corresponding values are shown in Table 5. The significance of the independent variable used in models 2 and 3 were also established using a partial *F*-test. The results are shown in Table 6. The effect of [S], [N] and

Table 6
Statistical significance of models 2 and 3 parameters ($n = 17$; $p = 4$)

Parameters	Degree of freedom	SSE	$R(M_1/M_2)$	MSE	F	p -Value
Model 2						
Full	12	7.16		0.6		
S	1	14.9	7.74	7.74	12.9	0
N	1	10.67	3.51	3.51	5.9	0.022
H	1	37.9	30.7	30.7	51.5	0
O	1	8.7	1.54	1.54	2.6	0.12
Constant, $k_{Cr(VI)}$	1	69.3	62.1	62.1	104.1	0
Model 3						
Full	12	4.1		0.34		
S	1	12.4	8.3	8.3	24.3	0
N	1	47.8	43.7	43.7	127.9	0
H	1	28.0	23.9	23.9	69.9	0
O	1	4.14	0.04	0.04	0.12	0.37
Constant, $k_{Cr(III)}$	1	74.3	70.2	70.2	205.5	0

[H] are statistically significant in both Cr(VI) adsorption (model 2) and reduction (model 3) models. However the effect of [O] is only slightly significant in the adsorption-model (model 2) and is insignificant in the reduction-model (model 3). The effect of oxygen concentration at the level found in the activated carbons in this study is low in comparison to the other heteroatoms, which may explain the lack of correlation between the Cr(VI) adsorption and the oxygen content of the carbon. Model 3 was modified by excluding the [O] parameter to generate model 4:

$$\text{Model 4: } \text{Cr(VI)}_{\text{reduced to Cr(III)}} = k_{Cr(III)}[S]^\eta[N]^\mu[H]^\kappa \quad (13)$$

The fitted parameter constants η , μ , κ for model 4 are reported in Table 7. Regression analyses of the fitted and experimental data are shown in Figs. 4 and 5. The Cr(VI) adsorption and reduction to Cr(III) fitted models showed regression correlations of 0.95 and 0.97, respectively, suggesting good fit of both sets of data. The goodness of fit of models 2 and 4 were further analysed using the adjusted- r^2 and mean square error to account for the bias with the number of parameters used in these models. Model 2 error parameters are adjusted- $r^2 = 0.94$ and $s_e = 0.6$ and model 4 are adjusted- $r^2 = 0.96$ and $s_e = 0.49$. These statistical parameters suggest models 2 and 4 adequately describes the correlation between the heteroatom concentration in the carbon and their corresponding Cr(VI) adsorption and reduction properties.

The role of heteroatom site densities in the removal of chromium by both adsorption and reduction to Cr(III) are analysed in Figs. 6 and 7. Chromium removal by adsorption and reduction are plotted as a function of the sum of [S] and [N] in Fig. 6 and to [H] in Fig. 7. Table 6 suggests [O] has little effect in the chromium reduction; as such it was not included in this

Table 7
Parameters of the modified chromium reduction model (model 4) [Cr(VI) reduction to Cr(III)]

Parameters	Values
$k_{Cr(III)}$	12867
η	0.48
μ	2.67
κ	-0.73

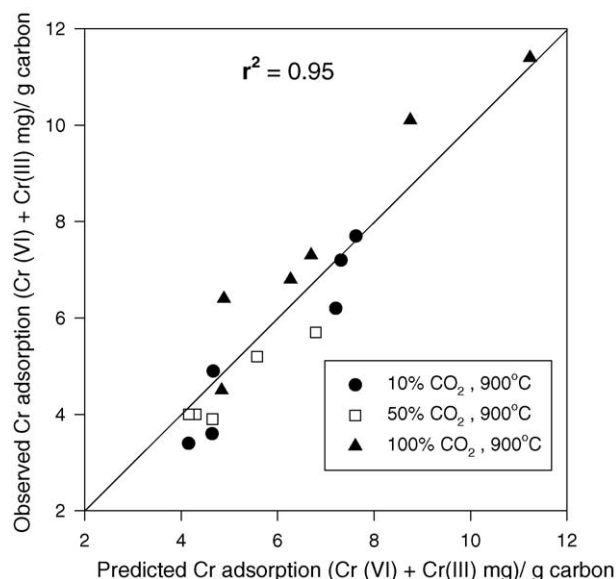
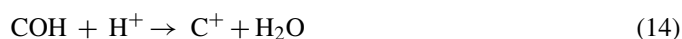


Fig. 4. Regression correlation of fitted model 2 and experimental Cr(VI) adsorption: (●) 10% CO₂, 900 °C; (□) 50% CO₂, 900 °C; (▲) 100% CO₂, 900 °C.

analysis. If the effect of the heteroatoms in the carbon pH as suggested by Figs. 3 and 4 are to be considered, the sum of [S] and [N] provides quantification of basic sites and [H] the acidic sites in the activated carbon. It is apparent that increasing the sulfur and nitrogen sites (see Fig. 6), promotes both the adsorption and reduction of chromium. The enhanced chromium adsorption provided by both increasing sulfur and nitrogen sites is consistent with the perceived electrostatic interaction arising between the chromium complex and the surface acidity of the carbon predicted by model 1. Bi-chromate ions (HCrO_4^-) will be the most stable species at low concentration (5 ppm) of chromium and at the pH (2) as used in this study. Basic sites are known to dissociate in water as follows [41,43]:



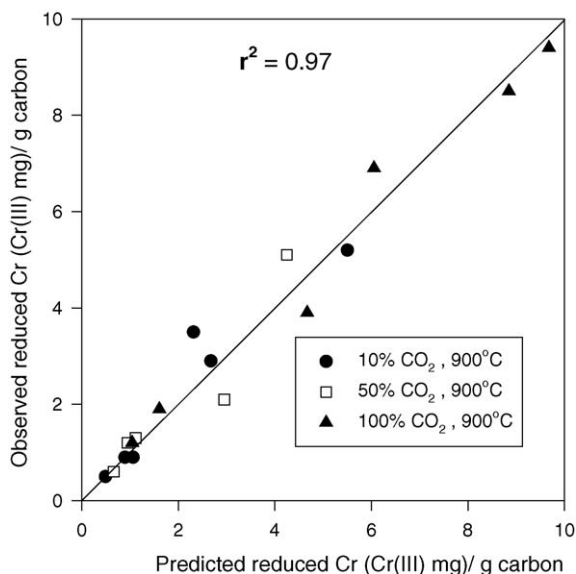


Fig. 5. Regression correlation of fitted model 3 and experimental reduction to Cr(III): (●) 10% CO₂, 900 °C; (□) 50% CO₂, 900 °C; (▲) 100% CO₂, 900 °C.

The adsorption of bi-chromate ions will be promoted onto these positive sites:



The sulfur and nitrogen sites which promote H-carbon surfaces produce alkaline suspensions and positive zeta potentials indicative of positively charged surfaces. Thus carbons containing sulfur and nitrogen demonstrate affinities for chromium anions. Acidic carbons dissociate by

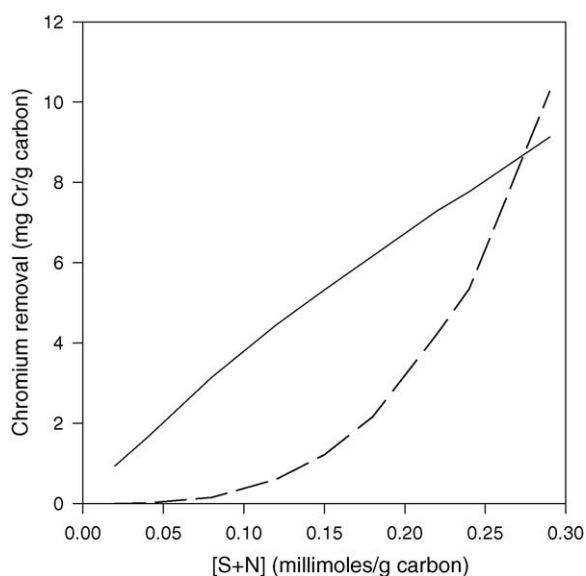


Fig. 6. Predicted Cr(VI) adsorption and reduction as a function of the ratio [S]+[N] site densities: (—) chromium adsorption (mg Cr/g), (---) Cr(VI) reduction to Cr(III) (mg Cr/g carbon), [H]=10 mmol/g carbon, [O]=10 mmol/g carbon.

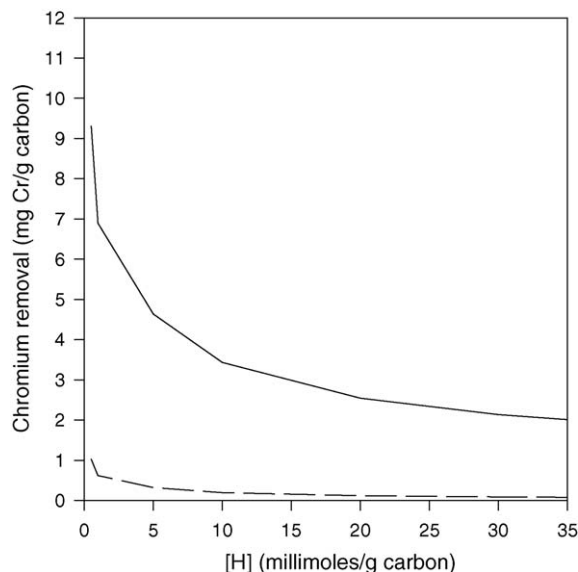


Fig. 7. Predicted Cr(VI) adsorption and reduction as a function of [H] site densities: (—) chromium adsorption (mg Cr/g), (---) Cr(VI) reduction to Cr(III) (mg Cr/g carbon), [S]=0.05 mmol/g carbon, [N]=0.1 mmol/g carbon, [O]=10 mmol/g carbon.

These carbons produce acidic suspension and negative zeta potential or negatively charged surfaces. Fig. 7 shows that increasing the hydrogen concentration reduced the adsorption and reduction of Cr(VI). The reduced adsorption is consistent with greater acidity of the carbon surface from higher hydrogen sites, as suggested in Fig. 3. According to Eq. (5), acidic surfaces generate negatively charged carbon surfaces which would repel the anionic chromium complexes. It is also apparent that the increased hydrogen sites provide an oxidizing environment. The oxygen sites, by the nature of its contribution to the acidity of the carbon will have similar effect in chromium removal.

The greater reduction of Cr(VI) to Cr(III) in the presence of higher sulfur and nitrogen sites is also shown in Fig. 6. This behaviour is consistent with the basic character of these sites which according to the Lewis base concept would provide a higher concentration of delocalized electrons that would promote a reductive environment. The Cr(VI) reducing abilities of the sulfur and nitrogen sites, present, in the activated carbons in this study are also consistent with observed reducing properties or the abilities of sulfur compounds such as FeS, H₂S and S₂O₃²⁻ to donate electron [44,45]. Similarly the ability of nitrogen groups bonded with carbon to act as reductants are also well established. Chebrou et al. [46] reports a class of aliphatic amides which effectively reduced organic nitrogen compounds. Nishiyama et al. [47] used immobilized amide groups on chitosan to reduce ethyl benzoylformate.

Comparing the relative effects of heteroatom sites to chromium removal in Fig. 6, it is apparent that the adsorption effect is more prevalent at the lower [S] and [N] sites in comparison to the reduction of chromium. The combined [S]+[N] sites, as suggested by Fig. 6, must be maintained at values lower than 3.3 mmol [S]+[N]/g carbon to promote adsorption rather than reduction. Fig. 7 shows the effect of [H] site densities in chromium adsorption is not as significant as that of

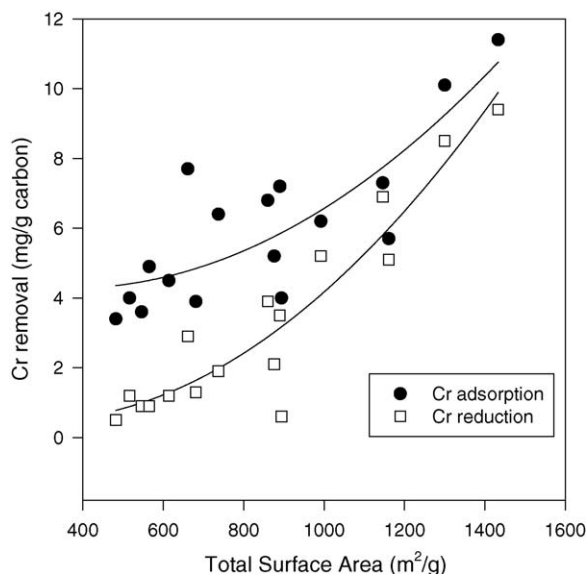


Fig. 8. Effect of total surface area in the removal of chromium by adsorption and reduction.

chromium reduction and that optimal removal by adsorption will be achieved at the higher hydrogen site densities.

In considering these results, it appears optimal chromium adsorption is achieved in carbon with basic surfaces imparted by having nitrogen and sulfur sites. However these sites must be maintained at values that will not exacerbate chromium reduction that potentially competes with the removal of chromium by adsorption. The presence of high hydrogen sites, can significantly minimize chromium reduction whilst maintaining adequate chromium adsorption. Table 2 suggests these required carbon properties can be achieved from bagasse precursor activated by physical activation.

It is apparent from Fig. 6 that the dual effects of heteroatoms in chromium removal are counteracting. This aspect can clearly complicate the design of adsorbents with optimal chromium adsorption capacities. This study has shown the insight provided by the proposed empirical models 2 and 4 on the roles of the heteroatom concentrations can be used as a basis to design the carbon surface chemistry that would demonstrate high chromium adsorption.

3.7. Effect of textural properties of carbons in the removal of chromium

Although the main focus of this study was the role of the surface chemistry of the carbons in chromium removal from solutions, the textural properties of the carbon can also have an important effect in heavy metal adsorption. The effects of carbon total surface areas in chromium removal are shown in Fig. 8. As shown, increasing the total surface area of the carbon increased both the adsorption and reduction of chromium. Although chromium adsorption is relatively higher in comparison to chromium reduction for all the carbon tested, it is apparent that this difference is reduced at the higher surface area. Since adsorption and reduction are both surface effects,

it is not unusual for these phenomena to increase with the textural development of the carbon. These results suggests that in addition to the control of the carbon surface towards a basic characteristics, the choice of the textural properties of the carbon is also required to optimise chromium removal from solution.

4. Conclusions

Heteroatoms are found to affect the surface acidity and reductive environment in solution provided by activated carbon from bagasse. The basic surface imparted by sulfur and nitrogen sites is proposed to be associated with Lewis base characters of these groups in the activated carbon. These groups provide reductive environments which is consistent with strong delocalization of electrons in Lewis base groups. The effect of the sulfur and nitrogen heteroatoms in the surface acidity and reductive properties of the carbons control the removal of Cr(VI) from solutions. The basic sites of sulfur and nitrogen groups provide positively charged carbon surface which assist in adsorbing the anionic chromium complex. Both the oxygen and hydrogen sites provide acidic surfaces and promote an oxidizing environment. The repulsion of bichromate ions by the net negative charge imparted by hydrogen and oxygen sites are not as significant compared to the reductive effects of these sites to chromium adsorption. As such optimal chromium removal will be achieved in carbons containing high hydrogen and oxygen sites. This study suggests the presence of naturally occurring nitrogen in bagasse makes it a suitable precursor for preparing basic carbons. Although these heteroatoms are present in low quantities (<1 wt.%), it is apparent from this study that excessive loading of heteroatoms may have little merit in effecting the adsorption of heavy metals. In fact, it appears that high nitrogen and sulfur loading may contribute to significant reduction of chromium to Cr(III) thus reducing Cr(VI) removal by adsorption. The use of low temperature chemical carbonization with sulfuric acid is also useful in fixing sulfur onto the carbon surface which would also contribute to the basicity of the carbon. This study has also shown that increasing the total surface of the carbon enhances both the adsorption and reduction of chromium. Optimal removal of chromium from solution will also depend on suitable choice of carbon textural properties.

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