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A COMPARATIVE STUDY OF THE PERFORMANCE OF SOUTH AFRICAN COAL FLY ASH AND CARBONACEOUS ADSORBENTS IN THE REMOVAL OF MELANOIDIN FROM WASTEWATER

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Abstract

Melanoidin is an antioxidant compound found in among others, effluents from molasses distilleries and fermentation industries. Being recalcitrant, biodegradation alone does not remediate its attendant problems including offensive odour, dark colour and high oxygen demand. It is therefore imperative that alternative treatment methods such as adsorption are explored to help mitigate these problems. In this paper, efficiency of low cost South African coal fly ash (SCFA) as compared to two commercial activated carbons for removal of melanoidin has been reported. Batch adsorption of synthetic melanoidin was carried out using Chemviron activated carbon; Norit activated carbon and SCFA. Influence of temperature, sorbent mass and initial concentration on melanoidin removal efficiency was evaluated for each sorbent. An increase of temperature slightly enhanced sorption by all sorbents. Sorbent dosage of 3 g/100 mℓ of Norit activated carbon was able to achieve 100% decolourization of solution with an initial concentration of 5930 mg/ℓ. On the other hand, 10 g/100 mℓ of Chemviron carbon attained 100% removal efficiency, while 25 g /100 mℓ of SCFA only achieved 71% decolourization. Non-linear error optimization was used to fit data onto sorption isotherm models. Freundlich isotherm gave the best fit for Norit carbon, while Redlich-Peterson fitted the data better for SCFA and Chemviron carbon. Although SCFA had the least sorption capacity at 53.6 mg/g compared to that of Norit at 976 mg/g, it is a cheaper option that could be applied in treatment of melanoidin containing effluent.
Keywords: Activated carbon, Adsorption, Melanoidin, South African Coal fly ash

INTRODUCTION

Effluents from fermentation processes that use molasses as carbon source, such as those generated in ethanol production, bakery yeast processing, and brewery industry contain melanoidin, a brown antioxidant compound which is hardly biodegradable. Sugar processsing also results in effluent containing melanoidin, caramels and melanin [1], which are offensive to the environment. Because of their antioxidant properties, melanoidins are toxic to typical aquatic micro and macro-organisms.

The melanoidin is formed by the interactions between carbohydrates (carbonyl groups) and amino acids or proteins (free amino groups) in a non-enzymatic condensation process called Maillard reaction. The structure of the melanoidin is not fully understood and is dependent on

the nature and concentrations of the parent compounds, and reaction conditions such as pH, temperature, heating time and solvent system, making it difficult to quantify these compounds [2], [3], [4]. However, since natural and synthetic melanoidins both have similar elemental (CHON) compositions, spectroscopic properties and electrophoretic mobilities at various pH values [3], most investigations about them have been carried out using the synthetic melanoidin.

Conventional biological processes such as activated sludge treatment process are insufficient to treat melanoidin containing wastewater released from distilleries and fermentation industries [5], [3]. Only 6%–7% degradation of the melanoidins has been achieved in the conventional anaerobic–aerobic effluent treatment processes [6], hence, alternative treatment processes have been explored. Various methods have been applied, with each reporting different success rate. Electrochemical method attained decolourization efficiency of 88.31 % and COD reduction of 39.66% for a distillery spent wash containing melanoidin [7]. However, even though this method guarantees high treatment efficiency, its effectiveness depends on the type of electrodes, the construction of electrocoagulators and the condition under which the process is run. It could also be expensive since the cost of replacement of electrodes such as the titanium substrate insoluble anode might be high. On the other hand, coagulation using *Moringa oleifera* seeds resulted in a decolourization efficiency of about 53% for molasses spent wash [8]. But due to it antimicrobial activity, it might be counterproductive in cases where treatment process is inclusive of biodegradation. Other coagulants such as alum have been shown to cause Alzheimer's disease and might not be so attractive to treatment of melanoidin containing water streams. Also, 82% of dissolved organic carbon was removed from a synthetic melanoidin solution after 4 hours of chemical (H_2O_2) oxidation followed by 7 days of aerobic biodegradation [9]. This method however might be expensive as well since the running cost of the chemicals could be high, apart from the fact that highly trained personnel is needed for the operation of the advanced oxidation process [10]. Moreover, membrane treatment coupled with biodegradation was reported to have reduced molasses spent wash chemical oxygen demand (COD) by only 41%. It was postulated that most of the removed COD consisted of low molecular weight compounds while the high molecular weight compounds such as melanoidin remained unaffected [11]. For these reasons, other remediation processes such as adsorption continue to be explored for their effectiveness.

Adsorption process has been used in the current study due to its inherent robustness. Choice of sorbent type depends on its suitability to treat a given waste stream, its cost and availability. Activated carbon adsorption has been cited by the US Environmental Protection Agency as one of the best available environmental control technologies, especially for organic compounds [12] and hence has been used to benchmark the current study. On the other hand, South African Coal fly ash is cheap and is readily available and its efficacy on decolourization of melanoidin containing wastewater needs exploration. The nature of fly ash is influenced by, amongst others, the origin of the coal and the burning conditions under which it was formed. It is therefore reasonable to expect South African coal fly ash to behave differently from those in other parts of the world. This uniqueness of coal fly ash properties with place of origin makes it a candidate for investigations, even though coal fly ash has been successfully used for sorption of distillery spent wash elsewhere [13]. Melanoidin removal efficiency of the two commercial activated carbons, Norit and Chemviron, were compared to that of South African coal fly ash (SCFA). Performance comparison amongst the three sorbents was undertaken with the view to qualify SCFA and activated carbon as suitable for melanoidin removal from wastewaters, cost and availability being taken into account.

Nomenclature

1/n	Freundlich constant indicative of adsorption intensity
Abs_f	Final absorbance of melanoidin solution.
Abs_o	Initial absorbance of melanoidin solution at 475nm
a_R	Redlich-Peterson isotherm parameter (ℓ/mg)
ARE	Average relative error
C_e	Melanoidin concentration at equilibrium (mg/ℓ)
C_o	Synthetic melanoidin concentration, assuming all reactants got converted to melanoidin at the end of reaction (mg/ℓ)
EABS	The sum of absolute errors
HYBRID	The hybrid fractional error function
k_f	Freundlich constant indicative of sorption capacity (ℓ/g)
K_L	Langmuir adsorption constant (ℓ/mg)
K_R	Redlich-Peterson the isotherm parameter (ℓ/g)
m	Mass of activated carbon (g)
MPSD	Marquardt's percent standard deviation
q_e	Melanoidin uptake at equilibrium (mg/ℓ)
q_m	Langmuir parameter, maximum sorption capacity (mg/g)
R	Universal gas constant (8.314J/mol.K)
R^2	Linear coefficient of determination
R_L	Langmuir separation or equilibrium parameter
SSE	The sum of squares of errors
V	Volume of melanoidin solution (ℓ)
β	Redlich-Peterson isotherm parameter.

MATERIALS AND METHODS

Melanoidin Preparation

Melanoidin was prepared by mixing 4.5 g of glucose (G8270 D-(+), Sigma-Aldrich), 1.88 g of glycine (G7126, reagentplus TM>=99%, Sigma-Aldrich) and 0.42 g of sodium bicarbonate with 100ml of distilled water and then heated for 7 h at 95 ^{o}C. After heating, 100ml of water was added [14]. The prepared solution had a chemical oxygen demand (COD) value of 29,160 mg/ ℓ from which dilute solutions of melanoidin were prepared. For pH adjustment, 0.1M NaOH and 0.1M HCl were used.

Sorbents

Three adsorbents were used for the sorption of synthetic melanoidin: granular activated carbon, (ENVIRONCARB^{TM} 207C 4 X 8 from Chemviron Carbon) (Chemviron); South African coal fly ash (SCFA) and pelletized activated carbon (NORIT 0.8, USA) (Norit). Prior to use, each of the sorbents were washed several times with distilled water and dried at 100^{o}C for 24 hours. Some properties of the activated carbon are as listed in **Error! Reference source not found.**. The SCFA was obtained from Lethabo Power Station in South Africa and characterized by X-Ray diffractometer while its surface area was determined by use of Micrometrics (TriStar 3000) Surface Area and Porosity Analyzer.

Table 1: Properties of carbon		
Characteristics	Norit	Chemviron
Particle form (-)	Pellets	Granular
Partitcle size (mm)	1	3.5
Iodine number (-)*	1000min	1100
Molasses Number*	450 max	450 max
Unit surface area (m^2/g)*	900 ±50	1100
Apparent bulk density *(g/cm^3)	0.53	0.51

*From the manufacturer

Equilibrium Experiment

Each of the sorbents was accurately weighed and added into 100 m ℓ of melanoidin solution in a 200m ℓ bottle. The mixture was agitated at 200 rpm in a shaker at constant temperature for 24 hours. This was done for three different temperatures: 298K; 308K and 318K. Samples were then filtered using Whatman 42 filter paper and concentrations determined from the absorbance of the solutions at wavelength 475nm [9] using Pharmacia Biotech Ultraspec 3000 UV-Visible spectrophotometer. Readings were taken in duplicate for each solution to check on repeatability and average values recorded.

Percentage color removal was calculated using the formula:

$$R_t\% = \frac{Abs_o - Abs_f}{Abs_o} \times 100 \qquad [1]$$

where Abs_o is the initial absorbance while Abs_f is the final absorbance.
Melanoidin uptake was calculated by:

$$q_e = \frac{(C_o - C_e)V}{m} \qquad [2]$$

where q_e is the specific uptake in mg/g at equilibrium, C_o and C_e are the initial and final concentration in mg/ ℓ, respectively, V is the volume in litres of melanoidin solution and *m* is the mass of activated carbon in grams.

RESULTS AND DISCUSSIONS

Sorbent characterization

X-ray diffraction analysis for the SCFA revealed that it consisted mostly of mullite ($Al_6Si_2O_{13}$), quartz (SiO_2), a small amount of hematite (Fe_2O_3) and calcium oxide (CaO) with large characteristic peaks of quartz (SiO_2) as shown in Figure 1[15] . The X-ray diffraction studies were carried out using an X-ray diffractometer (PANalytical, Philips PW 1710) with Cu Kα radiation at 40 kV and 50 mA. The X-ray pattern was recorded for 2θ from 10° to 65° at a scan rate of 1.2° min^{-1}.

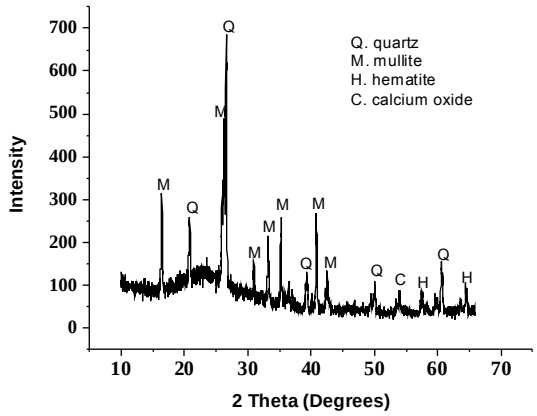

Figure 1: XRD pattern for coal fly ash

Specific surface area (S_{BET}) of 1.7287 m²/g and pore volume of 0.002245cm³/g for SCFA was determined from the adsorption-desorption isotherm of nitrogen at -196 ˚C using the Micrometrics (TriStar 3000) Surface Area and Porosity Analyzer. Using the same method, the specific surface area (S_{BET}) was found to be 1057.0368 m^2/g and 967 m^2/g for Norit activated carbon and Chemviron activated carbon respectively.

Effect of Sorbent Mass on Decolourization Efficiency

Effect of sorbent mass on the removal efficiency of the synthetic melanoidin was investigated at a temperature of 298 K for masses between 0.5 g and 25 g. These were used to contact 100 mℓ of melanoidin solution over 24 hour period. Initial concentration of the melanoidin solution was 5930 mg/ℓ while the initial pH was around 7. Figure 2 shows that increasing masses for the three sorbents generally increased removal of melanoidin. This is due to the increased availability of sorption sites as mass is increased. As evident from Figure 2, Norit activated carbon showed the best performance. Only 3 g of the Norit activated carbon was able to remove 100 % of the melanoidin, as compared to 10 g of Chemviron activated carbon. Norit activated carbon used had a particle size of 1 mm, while Chemviron activated carbon had a particle size of 3.5 mm and this size difference could have partly contributed to the variation in their performance, since diffusion path is lesser for smaller sized particles. On the other hand, 25 g of SCFA was only able to remove 71.7 % of melanoidin. This huge variation can be attributed to the low specific surface area of SCFA of 1.7 m^2/g, as compared to around 1000 m^2/g for the carbons as this presented fewer sorption sites. For further experiments, 1 g, 3 g and 5 g of Norit, Chemviron and SCFA, respectively, were used for every 100 mℓ of melanoidin solution because beyond such sorbent mass, only marginal increase of melanoidin removal efficiencies were realized.

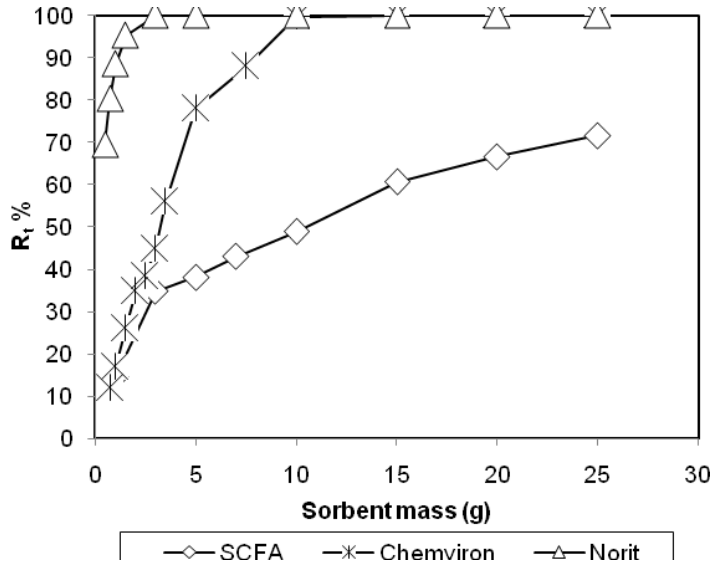

Figure 2: Effect of sorbent mass on removal efficiency (Temp 298 K; Initial concentration 5930 mg/ ℓ; Initial pH 7)

Influence of Initial Concentration of Solution

Decolourization efficiency depended on the concentration of the initial solution. This was investigated by contacting 1 g of Norit, 3 g of Chemviron and 5 g of SCFA for a period of 24 hours with 100 mℓ of melanoidin solutions, at various concentrations ranging from 305 mg/ℓ to 7469 mg/ℓ at a temperature of 298 K. As evident from Figure 3, there was a general trend of reduced efficiency as initial concentration increased. A given sorbent mass has limited sorption sites, which after being occupied will not be able to adsorb any more melanoidin, hence the reduced decolourization efficiency with increasing initial concentration. On the other hand, sorption capacity for the three sorbents increased as initial concentration was increased. This is due to enhanced sorption driving force with increased initial concentration. Again, Norit activated carbon outperformed the other two sorbents with better decolourization efficiency and sorption capacity. For instance for initial concentration of 2843 mg/ℓ, Norit had a sorption capacity of 262.1 mg/g, while Chemviron and SCFA had sorption capacities of 41 mg/g and 21.8 mg/g, respectively. Even though SCFA had the least sorption capacity, it is abundantly available in South Africa and by increasing it dosage, acceptable decolourization efficiency can be attained. This is illustrated by Figure 3, where using 5 g of SCFA against 3 g of Chemviron resulted in almost equal decolourization efficiencies.

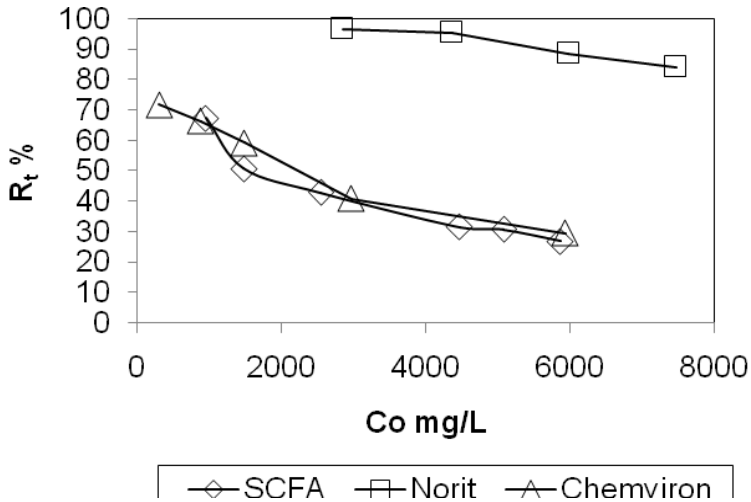

Figure 3 : Effect of initial concentration of solution on decolourization efficiency (Temp 298 K; Sorbent masses, 3 g Chemviron, 1 g Norit, 5 g SCFA; pH 7)

Effect of Temperature

Effect of temperature on equilibrium sorption capacity was studied in the temperature range of 298 K - 318 K for all the sorbents. In each instance, 1 g of sorbent was used to remove melanoidin from 100 mℓ of solution with initial concentration of 5930 mg/ℓ and pH 7. Increase of temperature slightly enhanced sorption of melanoidin on all of the three sorbents as shown in Figure 4. Equilibrium sorption capacity increased from 530 mg/g to 580 mg/g for Norit activated carbon following an increase of temperature from 298 K to 318 K. Likewise, sorption capacity for Chemviron activated carbon increased from 98 mg/g to 143 mg/g while that of SCFA increased from 47 mg/g to 87 mg/g following an increase in temperature from 298 K to 318 K. The enhanced sorption may be as a result of an increase in the mobility of the solutes molecule with an increase in their kinetic energy, and the enhanced rate of intra-particle diffusion of sorbate with the rise of temperature. The increase could also be attributed to endothermic nature of the processes.

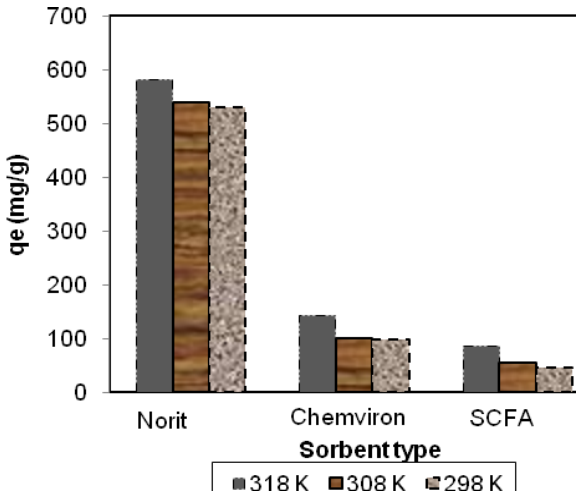

Figure 4: Effect of temperature on sorption capacity (Initial concentration: 5930 mg/ ℓ; Sorbent mass 1 g; pH 7)

Adsorption Isotherms

Several mathematical models can be used to describe experimental data of adsorption isotherms. The equilibrium data were modeled with the Langmuir, Freundlich and Redlich-Peterson models. Non-linear regression analysis was used to determine the isotherm model parameters indicated in Table 2. These parameters were determined by minimization of five non-linear statistics: SSE; HYBRID; MPSD; ARE and EABS as described by Allen et al. [16]. Sum of normalized errors (SNE) was obtained and used as an indicator as to which isotherm had the best fit to experimental equilibrium data. A summary of the errors associated with the three isotherm models studied for different sorbents is shown in Table 3.

Langmuir Isotherm is described by [17]:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \qquad [3]$$

where qe (mg/g) is melanoidin uptake at equilibrium, q_m (mg/g) is the Langmuir maximum sorption capacity, K_L (ℓ/mg) is Langmuir adsorption constant and C_e (mg/ℓ) is the concentration at equilibrium.

It assumes a number of factors: monolayer sorption on a set of distinct localized sorption sites; no interaction between sorbed species; all sites are energetically equivalent; the adsorbent is structurally homogeneous among others. For all the sorbent, non-linear optimization resulted in lower SNE values as compared to linear regression. However, compared to other models, it had highest SNE values for all the three sorbents as indicated in Table 3, hence was not considered as the best fit for experimental equilibrium data. A comparison of Langmuir isotherm to the others is shown in Figure 5-7 for each of the three sorbents. As evident from Figure 5, 6 and 7, Norit activated carbon had higher sorption capacity followed by Chemviron activated carbon and lastly by SCFA.

Freundlich Isotherm

Freundlich isotherm is often used for heterogeneous surface energy systems and is represented by the equation [18]:

$$q_e = k_f C_e^{\frac{1}{n}} \quad [4]$$

where q_e (mg/g) is the equilibrium sorption capacity, k_f (ℓ/g) is Freundlich constant indicative of sorption capacity, C_e (mg/ℓ) is the equilibrium concentration and 1/n is the Freundlich constant indicative of adsorption intensity.

Freundlich model fitted experimental data the best for Norit activated carbon as indicated by the lowest SNE value in Table 3. Therefore, heterogeneous adsorption of melanoidin onto activated carbon is inferred. However, for SCFA and Chemviron, Freundlich isotherm was not the best fit, although it could be used as well to model the sorption equilibria. The magnitude of the Freundlich exponent, 1/n, is an indicator of the favourability of adsorption, with exponent values between 1 < n < 10 showing a beneficial adsorption. For all sorbents, 1/n values were below unity: 0.4271; 0.4025 and 0.3818 for Chemviron, Norit and SCFA, respectively, indicating favourability of the adsorption as well as implication that part of adsorption process could be chemical in nature [19].

Redlich-Peterson isotherm

The Redlich-Peterson isotherm contains three parameters and incorporates the features of the Langmuir and the Freundlich isotherms. It can be described as follows [20]:

$$q_e = \frac{K_R C_e}{1 + a_R C_e^{\beta}} \quad [5]$$

where K_R (ℓ/g), a_R (ℓ/mg) and β are the isotherm parameters.

It has two limiting cases: when β=1, the isotherm reduces to Langmuir type; and when β=0, the isotherm transform into a Henry's law equation [21]. It may be used to represent adsorption equilibria over a wide concentration range, and can be applied either in homogeneous or heterogeneous systems due to its versatility[19]. Redlich-Peterson resulted in better fit for Chemviron and SCFA as shown by the lowest SNE values in Table 3. Exponent β values of 0.8, 0.6, and 0.6 for Chemviron, SCFA and Norit respectively as shown in Table 2 shows that the adsorption process is favourable [22].

Table 2 Langmuir, Freundlich and Redlich-Peterson parameters for 298 K isotherms different sorbents							
Sorbent Type	Langmuir		Freundlich		Redlich-Peterson		
	K_L (ℓ/mg)	q_m (mg/g)	K_f (ℓ/mg)	n	K_R (ℓ/g)	a_R (ℓ/mg)	β
Chemviron	0.0015	62.029	1.685	2.3412	0.1252	0.0101	0.8027
SCFA	0.0005	53.5988	1.3298	2.6195	4.281	3.1791	0.6171
Norit	0.002	976.75	38.82	2.4846	119.01	3.1898	0.5906

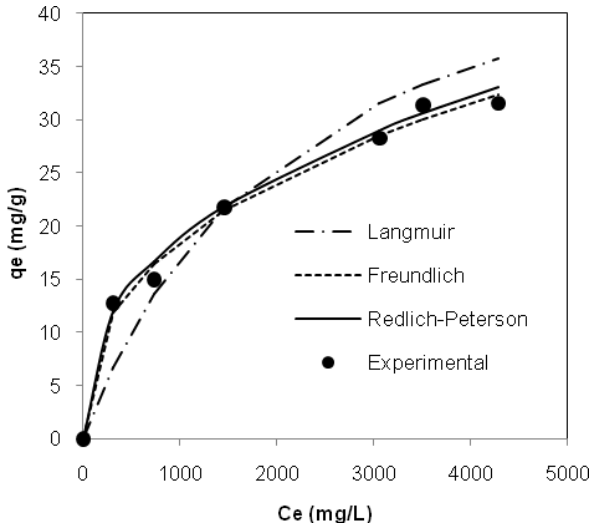

Figure 5: Sorption equilibrium curves for SCFA (temp 298 K)

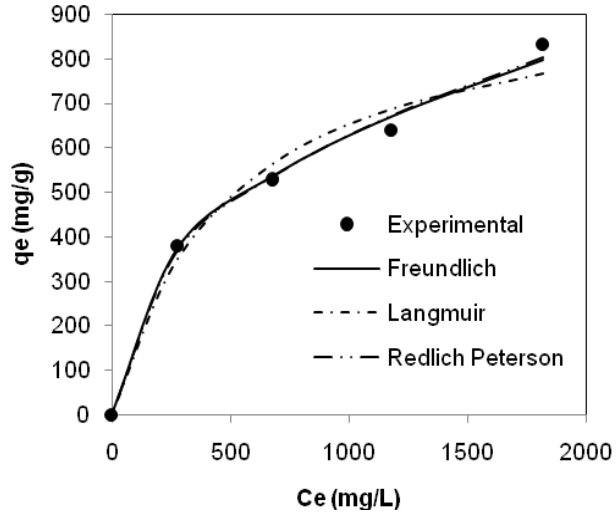

Figure 6: Sorption equilibrium curves for Norit (temp 298)

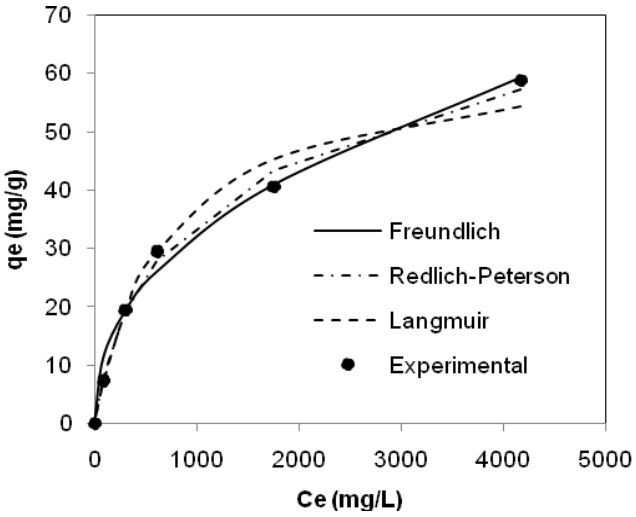

Figure 7: Sorption equilibrium curves for Chemviron (temp 298)

Table 3 Errors for different isotherms and sorbent types				
Sorbent Type	Error Function	Langmuir	Freundlich	Redlich-Peterson
Chemviron	SSE	47.9955	28.5064	14.5081
	HYBRID	33.0383	86.7700	21.0735
	MPSD	8.4330	32.3024	9.3091
	ARE	4.7383	14.0431	5.5014
	EABS	10.4182	8.7959	7.4486
	SNE	3	4.4382	**1.9400**
Norit	SSE	8575.7925	2227.8944	299.8087
	HYBRID	660.9238	306.2542	6.8288
	MPSD	14.8582	4.6661	3.1004
	ARE	7.4087	2.9251	3.1004
	EABS	176.9999	77.5855	77.5725
	SNE	5	**1.8704**	2.0067
SCFA	SSE	69.2191	5.5458	4.5861
	HYBRID	99.4526	9.5729	9.1305
	MPSD	25.6655	7.5067	7.6393
	ARE	14.6095	4.2882	3.8008
	EABS	16.8312	5.0291	4.1202
	SNE	5	1.0612	**0.9607**

Thermodynamics

Thermodynamic considerations of an adsorption process are necessary to conclude whether the process is spontaneous or not. Thermodynamic parameters: Gibbs free energy change ΔG^o; enthalpy ΔH^o, and entropy ΔS^o were obtained from the experiments carried out at

different temperatures: 298K, 308K and 318K. Thermodynamic parameters were calculated using the following equations:

$$\Delta G^\circ = -2.303RT \log K_L \quad [6]$$

$$Log K_L = \frac{\Delta S^\circ}{2.303R} - \frac{\Delta H^\circ}{2.303R}\left(\frac{1}{T}\right) \quad [7]$$

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

A plot of Log K_L against 1/T yields a straight line with the intercept of $\Delta S^o/2.303R$ and a slope of $\Delta H^o/2.303R$ from where the parameters are determined. The thermodynamic parameters are as given in Table 4. The negative values of the Gibbs free energy change for all the sorbents confirms the feasibility of the process and indicates spontaneous nature of sorption of melanoidin at all the temperatures studied. There was a decrease in the value of ΔG^o for all the three sorbents with an increase in temperature as shown in Table 4, indicating that the adsorption of melanoidin on the sorbents considered becomes more favourable with increasing temperature [23]. The positive values of ΔH^o for all the sorbents also point to the fact that the sorption processes were endothermic and physical in nature whereas the positive values of ΔS^o indicated increased randomness at the solid-solute interface during adsorption. The small values of ΔS^o suggest that no remarkable change in entropy occurred.

Table 4
Thermodynamic parameters for sorption of melanoidin for different sorbent

	Temp (K)	ΔG^o (KJ/mol)	ΔH^o (KJ/mol)	ΔS^o (J/mol.K)	R^2
Norit	298	-14.96			
	308	-17.98	75.00	301.88	0.9616
	318	-21.00			
SCFA	298	-8.67			
	308	-9.55	17.81	88.83	0.9858
	318	-10.44			
Chemviron	298	-8.74			
	308	-9.55	15.60	81.66	0.9851
	318	-10.37			

CONCLUSIONS

Comparative studies on the adsorption of melanoidin from wastewater showed that Norit activated carbon had the highest sorption capacity followed by Chemviron and lastly SCFA. Even though this makes the activated carbon a better choice as far as performance is concerned, it tends to be more expensive than alternative sorbents like SCFA, which are cheap and abundant, find more use in the removal of melanoidin from wastewater streams. The performance of the three sorbents was dependent on sorbent mass, initial concentration

of the solution and slightly on the temperature. Increase of temperature from 298 K to 318 K slightly enhanced removal efficiency for the three sorbents, implying possibility of physical adsorption. Whereas only 3g/100 mℓ of Norit activated carbon was able to achieve 100% decolourization of 100 ml melanoidin solution with 5930 mg/ℓ as initial concentration, 10 g/100 mℓ was need to achieve the same efficiency for Chemviron activated carbon. On the other hand, 25 g/100 mℓ of SCFA could only achieve 71.7% decolourization efficiency. However, since SCFA is readily available and cheap, it can be used for remediation of problems associated with melanoidin containing wastewater such as dark colour, offensive smell and high COD.

ACKNOWLEDGEMENTS

The authors would like to thank the International Foundation for Science (IFS) for financial support. V.O. Ojijo would also like to thank Tshwane University of Technology for granting him scholarship.

REFERENCES

1. H L Mudoga, H Yucel, and N S Kincal, Bioresource Technology, 99 p.3528 (2008)
2. S I F S Martins and M A J S v Boekel, Food Chemistry 83 p.135 (2003)
3. R Chandra, R N Bharagava, and V Rai, Bioresource Technology 99 p.4648 (2008)
4. V A Yaylayan and E Kaminsky, Food Chemistry, 63 p.25 (1998)
5. R P Evershed, H A Bland, P F V Bergen, J F Carter, M C Horton, and P A Rowley-Conwy, Science, 278 p.423 (1997)
6. T Gonzalez, M C Terron, S Yague, E Zapico, G C Galletti, and A E Gonzalez, Rapid Communications in Mass Spectrometry 14 p.1417 (2000)
7. R K Prasad and S N Srivastava, Chemical Engineering Journal 146 p.22 (2009)
8. R K Prasad, Journal of Hazardous Materials, 165 p.804 (2009)
9. J Dwyer and P Lant, Biochemical Engineering Journal, 42 p.47 (2008)
10. M Peña, M Coca, R González, R Rioja, and M T García, Chemosphere, 51 p.893 (2003)
11. Y Satyawali and M Balakrishnan, Journal of Environmental Management 86 p.481 (2008)
12. C Moreno-Castilla, Carbon 42 p.83 (2004)
13. R K Prasad and S N Srivastava, Chemical Engineering Journal, 146 p.90 (2009)
14. E C Bernado, R Egashira, and J Kawasaki, Carbon, 9 p.217 (1997)
15. V O Ojijo, M S Onyango, A Ochieng, and F A O Otieno, International Journal of Environmental Science and Engineering 2p.17 (2010)
16. S J Allen, Q Gan, R Matthews, and P A Johnson, Bioresource Technology, 88 p.143 (2003)
17. I Langmuir, Journal of American Chemical Society 38 (1916)
18. H M F Freundlich, Zeitschrift fur Physikalische Chemie, 57 p.385 (1906)
19. F Gimbert, N Morin-Crini, F Renault, P-M Badot, and G Crini, Journal of Hazardous Materials, 157 p.34 (2008)
20. O Redlich and D L Peterson, Journal of Physics Chemistry, 63 p.1024 (1959)
21. M Plavsic, B Cosovic, and C Lee, Science of The Total Environment, 366 p.310 (2006)
22. Z Aksu and E Kabasakal, Separation and Purification Technology, 35 p.223 (2004)
23. R Han, J Zhang, P Han, Y Wang, Z Zhao, and M Tang, Chemical Engineering Journal, 145 p.496 (2009)