

Decolourization of Melanoidin Containing Wastewater Using South African Coal Fly Ash

V.O. Ojijo, M.S. Onyango, Aoyi Ochieng and F.A.O. Otieno

Abstract—Batch adsorption of recalcitrant melanoidin using the abundantly available coal fly ash was carried out. It had low specific surface area (S_{BET}) of 1.7287 m^2/g and pore volume of 0.002245 cm^3/g while qualitative evaluation of the predominant phases in it was done by XRD analysis. Colour removal efficiency was found to be dependent on various factors studied. Maximum colour removal was achieved around pH 6, whereas increasing sorbent mass from 10g/L to 200 g/L enhanced colour reduction from 25% to 86% at 298 K. Spontaneity of the process was suggested by negative Gibbs free energy while positive values for enthalpy change showed endothermic nature of the process. Non-linear optimization of error functions resulted in Freundlich and Redlich-Peterson isotherms describing sorption equilibrium data best. The coal fly ash had maximum sorption capacity of 53 mg/g and could thus be used as a low cost adsorbent in melanoidin removal.

Keywords—Adsorption, Isotherms, Melanoidin, South African coal fly ash.

I. INTRODUCTION

MELANOIDINS are brown recalcitrant compounds present in the effluents of the fermentation processes that use molasses as carbon source, for instance those generated in ethanol production, bakery yeast processing, and brewery industry and are hardly biodegradable. These acidic nitrogenous polymers and co-polymers are a product of the Maillard reaction, a complex non-enzymatic browning reaction which occurs during the heating of sugars and amines [1]. The resulting carbon chain is a cyclic based structure with nitrogen bound in amine rather than nitro forms [2]. The formation of the brown colour is not fully understood and the structure of melanoidins is largely unknown [3], [4] which makes it difficult to quantify these compounds. Most of the studies about melanoidins have been done on model melanoidins, since natural and synthetic melanoidins both have similar elemental (CHON) compositions, spectroscopic properties and electrophoretic mobilities at various pH values [4].

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Melanoidins have antioxidant properties, which render them toxic to aquatic micro and macro-organisms and conventional biological processes such as activated sludge treatment process are insufficient to treat melanoidin containing wastewater released from distilleries and fermentation industries [5], [4]. 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.

Techniques that have been used with varying degree of success include among others: adsorption [7]; coagulation [8]; UV/ H_2O_2 oxidation [9]; electrochemical methods [10]; ozone oxidation [11]; membrane treatment [12]; and evaporation. Of these processes, adsorptive technique has been widely used because of its robustness. In a previous work, commercial activated carbon was reported to have achieved 92% colour reduction for 10g/L sorbent dose [7]. However, due to its high cost, alternative low cost adsorbents are finding more and more application. Coal fly ash from Neyveli Lignite Thermal Power Station at Neyveli showed great applicability for decolourization of molasses spent wash, with 91% colour reduction for 100g/L sorbent mass being reported [13]. In the current work, South African coal fly was used for the decolourization of synthetic melanoidin containing wastewater. 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 was the case with the removal and successful uptake of heavy metal ions from contaminated water by South African coal fly ash [14]. Since it is abundantly available and inexpensive, South African coal fly ash has been explored for its suitability for decolourization of melanoidin containing wastewater.

NOMENCLATURE

(Rt)	Percentage colour removal (%)
1/n	Freundlich constant indicative of adsorption intensity
Abs_f	Final absorbance of melanoidin solution.
Abs_0	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_0	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

II. MATERIALS AND METHODS

A. Sorbate

Melanoidin was prepared by mixing 4.5 g of glucose (G8270 D-(+), Sigma-Aldrich), 1.88 g of glycine (G7126, reagentplus TM $\geq 99\%$, Sigma-Aldrich) and 0.42 g of sodium bicarbonate with 100ml of distilled water and then heated for 7 h at 95 °C. After heating, 100ml of water was added [15]. The prepared solution had an initial chemical oxygen demand (COD) value of 16490 mg/L from which dilute solutions were prepared. The solutions' pH were adjusted by 0.1M NaOH and 0.1M NaCl.

B. Sorbent

The fly ash utilised in this investigation was an unclassified grade obtained from Lethabo Power Station in South Africa and collected using an electrostatic precipitator. This was washed with distilled water and dried at 105 °C in an oven for 24 hours before use.

The mineralogical composition of the fly ash was determined by the X-ray diffraction analyses for the qualitative evaluation of the common and predominant phases within the ash. X-ray diffraction studies were carried out using an X-ray diffractometer (PANalytical, Philips PW 1710) with Cu K α radiation at 40 kV and 50 mA. The X-ray pattern was recorded for 2 θ from 10° to 65° at a scan rate of 1.2° min⁻¹.

As evident from Fig. 1, the coal fly ash consists mostly of mullite (Al₆Si₂O₁₃), quartz (SiO₂), a small amount of hematite (Fe₂O₃) and calcium oxide (CaO) with large characteristic peaks of quartz (SiO₂). This composition is similar to that reported for fly ash investigated elsewhere for removal of various phenols from water [16].

The specific surface area (S_{BET}) of 1.7287 m²/g and pore volume of 0.002245 cm³/g were determined from the adsorption-desorption isotherm of nitrogen at -196 °C using the Micrometrics (TriStar 3000) Surface Area and Porosity Analyzer.

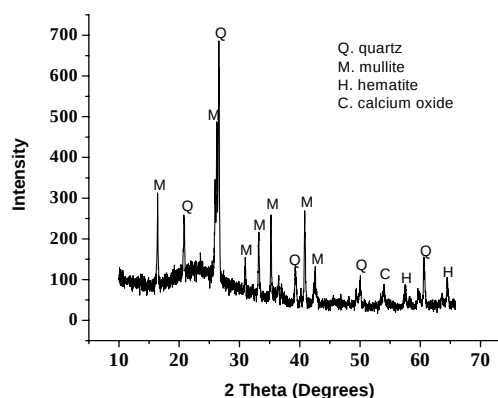


Fig. 1 XRD pattern for coal fly ash

C. Batch adsorption experiments

For each adsorption experiment, accurately weighed coal fly ash was added into 100 ml of melanoidin solution in a 200ml bottle. The mixture was agitated at 200 rpm in a thermostatic shaker 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 (R_t) was calculated using the formula:

$$R_t = \frac{Abs_o - Abs_f}{Abs_o} \times 100 \quad (1)$$

where Abs_o is the initial absorbance while Abs_f is the final absorbance.

Melanoidin uptake was calculated by:

$$q_e = \frac{(C_o - C_e)V}{m} \quad (2)$$

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 the volume in litres of melanoidin solution and m is the mass of coal fly ash in grams.

III. RESULTS AND DISCUSSIONS

A. Effect of Initial Concentration of Solution

As expected, it can be seen from Fig. 2 that increase of initial concentration decreases decolourisation efficiency. At a temperature of 298 K, increase of initial concentration from 946 mg/L to 5864 mg/L reduces decolourization from 67% to 26%. This is due to saturation of adsorption sites at higher concentrations.

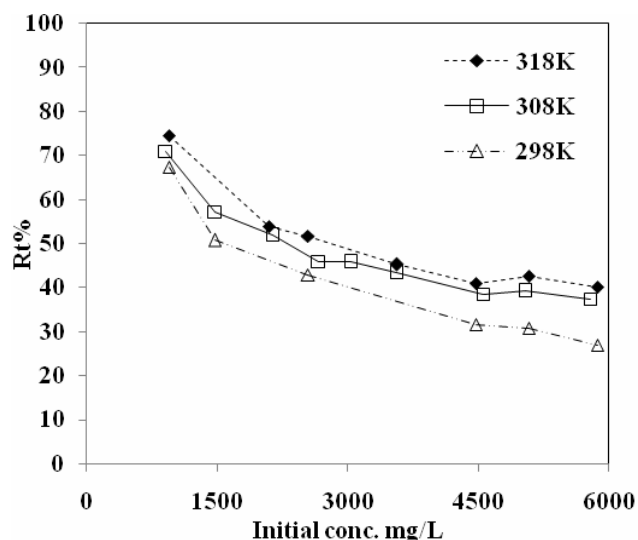


Fig. 2: Effect of initial sorbate concentration on colour removal (sorbent mass 5g; pH 7; particle size 106-150 mm)

B. Effect of sorbent mass

The effect of coal fly ash dosage on colour reduction was investigated for different initial concentrations, 1482 mg/L, 2951 mg/L and 5933 mg/L. As shown in Fig. 3, increasing the sorbent dosage enhanced colour reduction till around 15g for an initial concentration of 1482 mg/L. Beyond this dosage, there was only a marginal increase in colour reduction. The increase in colour reduction was due to increased availability of sorption sites as sorbent dose was increased. However, sorption uptake is reduced with increased sorbent dose. Increasing sorbent mass from 1 g to 25 g resulted in a decrease in sorption capacity from 38 mg/g to 5 mg/g for initial concentration of 1482 mg/L since there were increased sorption sites which remained unoccupied by the sorbate. Optimized sorbent dosage of 5 g as well as initial concentration of 1482 mg/L was then chosen for subsequent experiments.

C. Effect of Initial pH of Solution

The pH of solution is one of the most important parameters in the adsorption investigations. Different pH values (2 to 12) were studied for their effect on colour reduction at initial concentration of 1482 mg/L and a temperature of 298 K. As shown in Fig. 4, the optimum pH value for melanoidin removal was found to be around pH 6 with colour removal efficiency of 54%. However, for convenience of treatment of effluent to meet South African standards, the optimized pH was fixed at 7 for further studies.

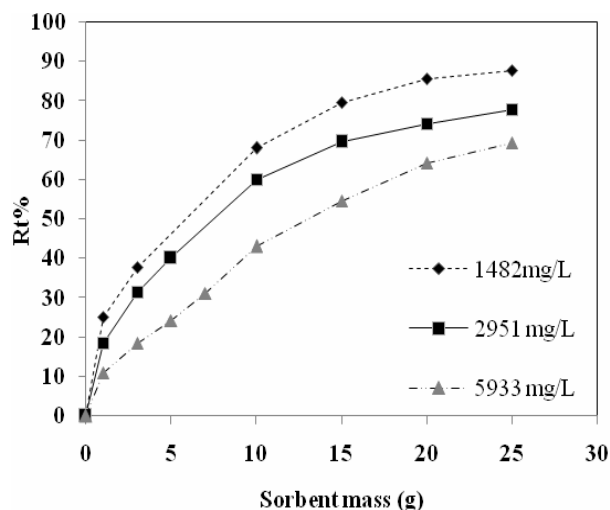


Fig. 3 : Effect of sorbent mass on colour reduction (temp 298K; pH 7; particle size 106-150mm)

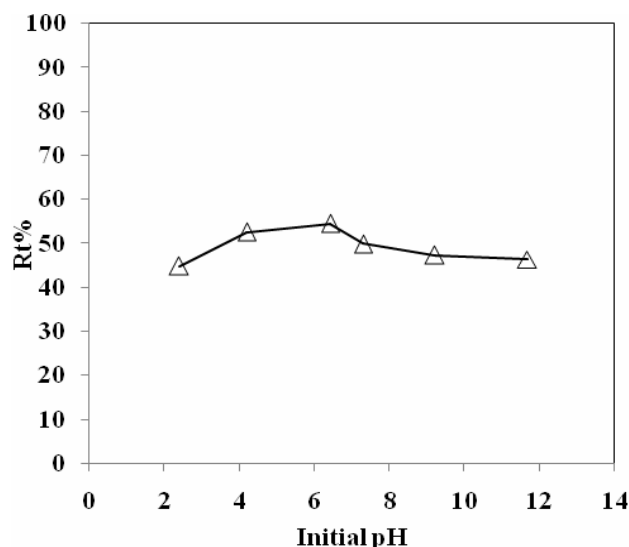


Fig. 4 : Effect of initial solution pH on colour removal (temp 298 K; initial conc. 1482 mg/L; sorbent mass 5 g; particle size 106-150mm)

D. Effect of Particle Sizes

Effect of particle sizes on colour removal was investigated for different initial concentrations. Particle sizes of 45 mm-53 mm; 53 mm-90mm; 90 mm-106 mm and 106 mm-150 mm were used. For these particle size ranges, the effect of the size on colour reduction was not profound as shown in Fig. 5. Sorbent of particle sizes between 106 mm- 150 mm was chosen for other experiments, since reduction of the size beyond this did not result in any better colour removal.

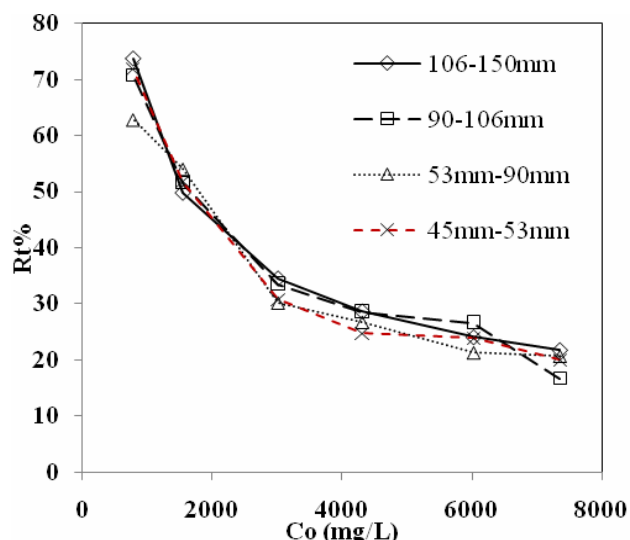


Fig. 5: Effect of particle size on colour reduction (temp 298 K; pH 7; sorbent mass 5 g; initial concentration 1482 mg/L)

E. Effect of Temperature

Effect of temperature on coal fly ash sorption capacity was studied for different initial concentrations. As shown in Fig. 6, increase of temperature increased sorption capacity for all the initial concentrations studied. This could be attributed to endothermic nature of the sorption process. For initial concentration of 2542 mg/L, sorption capacity increased from 30 mg/g to 47 mg/g as temperature was raised from 298 K to 318 K. The enhanced sorption may be as a result of an increase in the mobility of the solute molecules with an increase in their kinetic energy, and the enhanced rate of intra-particle diffusion of sorbate with the rise of temperature.

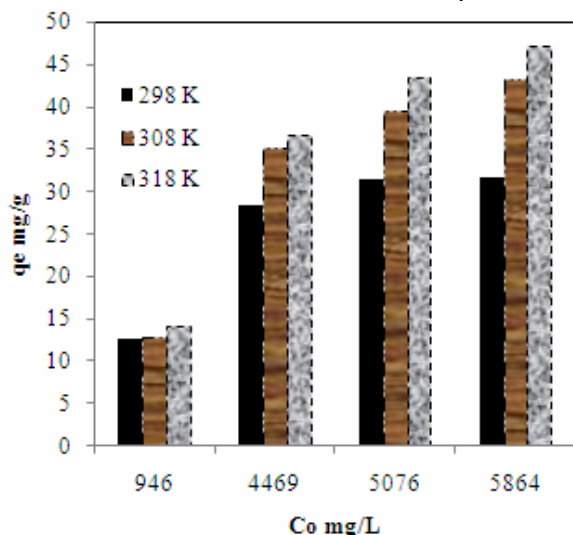


Fig. 6: Effect of temperature on sorption capacity (Sorbent mass 5 g; particle size 106-150mm; pH 7)

IV. ADSORPTION ISOTHERMS

The analysis of the equilibrium data by fitting them onto

different isotherm models is an important step to find the suitable model that can be used for design process. Three commonly used isotherm equations: Langmuir; Freundlich and Redlich-Peterson were used. Non-linear optimization method was used to determine the isotherm model parameters as listed in Table I. The parameters were determined by minimizing five non-linear statistics: SSE; HYBRID; MPSD; ARE and EABS as described by Allen *et al.* [17]. Sum of normalized errors (SNE) was obtained and used as an indicator as to which isotherm had the best fit to experimental equilibrium data. Table II shows a summary of the errors associated with the three isotherm models studied.

A. Langmuir Isotherm

Langmuir isotherm model 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 and is represented by [18]:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (3)$$

where q_e (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.

Minimization of HYBRID error resulted in better determination of Langmuir parameters for 298 K and 318 K isotherms. While for 308 K isotherm, SSE optimization resulted in lowest SNE value, hence a better determination of the parameters. Table I shows the Langmuir parameters for the three temperatures. Langmuir isotherm does not represent the best fit to experimental data as can be observed from the relatively larger error values in Table II.

B. Freundlich Isotherm

The well known Freundlich isotherm is often used for heterogeneous surface energy systems and is represented by the equation [19]:

$$q_e = k_f C_e^{\frac{1}{n}} \quad (4)$$

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 n is the Freundlich constant indicative of adsorption intensity.

Freundlich isotherm parameters obtained by optimization of error functions are as shown in Table I. For the three temperatures studied, HYBRID error minimization resulted in lowest SNE values. The isotherm model resulted in the best fit to experimental data for 318 K and 308 K since it had the lowest SNE values as shown in Table II. It could then be said that sorption of melanoidin onto the coal fly ash is heterogeneous. Likewise, since $1/n$ values are below unity for all the temperature, part of the sorption process could be chemical in nature [20]. Graphical comparison of the Freundlich isotherm to others for the three temperatures: 298

K; 308 K and 318 K are showed in Fig. 7, Fig. 8 and Fig. 9 respectively.

C. Redlich-Peterson Isotherm

Redlich-Peterson isotherm has three parameters featuring both the Freundlich and Langmuir isotherm equations and 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[20].

It is expressed as [21]:

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

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

It has two limiting cases: when $\beta=1$, the isotherm reduces to Langmuir type; and when $\beta=0$, the isotherm transform into a Henry's law equation.

Optimization of HYBRID error function resulted in lowest SNE values for 308 K and 318 K isotherms, whereas minimization of ARE gave the lowest value for the 298 K isotherm. Determined model parameters are as listed in Table I. Compared to other models, Redlich-Peterson was the best fit for experimental data for 298 K isotherm since it had the lowest SNE value as indicated in Table II. For 308 K and 318 K isotherms, error values from Redlich-Peterson were better than those from Langmuir model, even though they were slightly above those from Freundlich model. Therefore, it could be considered to represent the sorption equilibrium data. A graphical comparison to other models for 298 K, 308 K and 318 K isotherms is as shown in Fig. 7, Fig. 8 and Fig. 9 respectively.

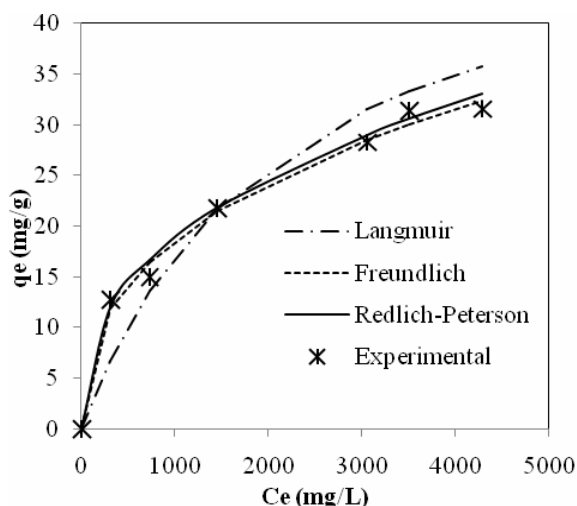


Fig. 7 Isotherms for melanoidin sorption onto coal fly ash (temp 298 K; pH 7; sorbent dose 5g; particle size 106-150 mm)

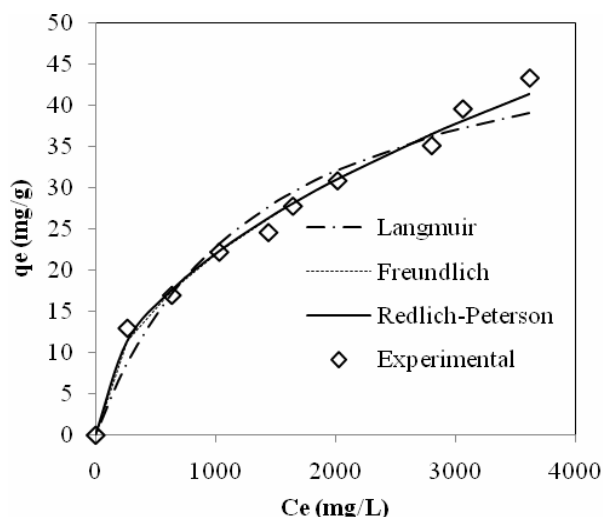


Fig. 8 Isotherms for melanoidin sorption onto coal fly ash (temp 308 K; pH 7; sorbent dose 5g; particle size 106-150 mm)

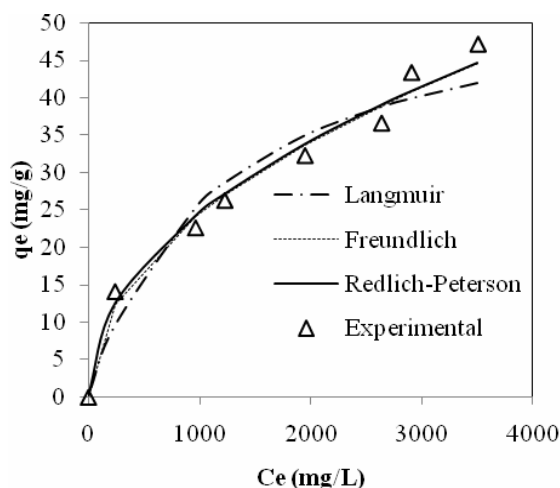


Fig. 9 (temp 318 K; pH 7; sorbent dose 5g; particle size 106-150 mm)

V. ADSORPTION THERMODYNAMICS

Thermodynamic consideration of an adsorption process is needed to conclude whether the process is favourable or not. Gibbs free energy change ΔG° , enthalpy ΔH° , and entropy ΔS° were obtained from the experiments carried out at different temperatures 298K, 308K and 318K. The relationship of these thermodynamic parameters with sorption equilibrium constant K_L is given by the equation [22]:

$$\ln K_L = \frac{-\Delta G^\circ}{RT} = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (6)$$

where ΔG° 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 $\ln K_L$ against $1/T$ yields a straight line with the

intercept of $\Delta S^\circ/R$ and a slope of $\Delta H^\circ/R$. The thermodynamic parameters as are given in Table III. The negative values of the Gibbs free energy change confirms the feasibility of the process and indicates spontaneous nature of sorption of melanoidin at all the temperatures studied. The value of ΔG° decreases from -8.67 kJ/mol to -10.44 kJ/mol, thus indicating that the adsorption of melanoidin on the coal

fly ash becomes more favourable with increasing temperature [23]. The positive value of ΔH° , 17 kJ/mol, points to the fact that the sorption process was endothermic, whereas the positive value of ΔS° , indicated increased randomness at the solid-solute interface during adsorption.

TABLE I
LANGMUIR, FREUNDLICH AND REDLICH-PETERSON CONSTANTS FOR MELANOIDIN ADSORPTION

Temp.	Langmuir		Freundlich		Redlich-Peterson		
	K_L (L/mg)	q_m (mg/g)	K_f (L/mg)	n	K_R (L/g)	a_R (L/g)	β
298 K	0.0005	53.5988	1.3298	2.6195	4.2810	3.1791	0.6171
308 K	0.0007	53.5988	0.7384	2.0351	3.5467	4.6763	0.5115
318 K	0.0008	56.2028	0.9109	2.0972	3.7658	4.0147	0.5264

TABLE II
SUMMARY OF ERRORS FOR VARIOUS TYPES OF ISOTHERMS

Temp	Error Function	Langmuir	Freundlich	Redlich-Peterson
318 K	SSE	83.8075	26.2041	26.4932
	HYBRID	64.0509	20.5221	20.8244
	MPSD	17.6983	8.9061	8.9946
	ARE	12.3045	6.2033	6.2563
	EABS	22.9954	12.7983	
	SNE	5	2.1970	2.2181
308 K	SSE	57.4369	13.6087	13.7904
	HYBRID	36.1939	8.7298	8.8688
	MPSD	14.2456	6.4867	6.5484
	ARE	8.7431	4.1029	4.1408
	EABS	18.9181	9.2874	9.3626
	SNE	5	1.8937	1.9133
298 K	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

Values in bold represents minimum sum of normalized errors (SNE)

TABLE III
THERMODYNAMIC PARAMETERS FOR SORPTION OF MELANOIDIN AT DIFFERENT TEMPERATURES

Temp (K)	ΔG° (KJ/mol)	ΔH° (KJ/mol)	ΔS° (J/mol.K)	R^2
298	-8.67			
308	-9.55	17.8	88.8	0.9858
318	-10.44			

VI. CONCLUSION

Sorption of melanoidin onto the South African coal fly ash was found to be dependent on various process variables as temperature, initial concentrations, initial solution pH and sorbent mass. Rising temperature favoured removal efficiency. pH 6 was found to be optimum while particle size ranges considered did not have any profound effect on colour reduction. Equilibrium adsorption showed the system followed Freundlich and Redlich-Peterson isotherms. With a maximum adsorption capacity of 53 mg/g, the South African coal fly ash can be successfully be used to decolourize melanoidin containing wastewater.

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