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SORPTION OF MELANOIDIN ONTO SURFACTANT MODIFIED ZEOLITE

Melanoidin is responsible for the dark brown color of distillery wastewater. Discharge of colored wastewater has a major environmental impact on the biota of the receiving water body. Consequently, this study explores the removal of melanodin from aqueous solution. The equilibrium, kinetics and thermodynamics of melanoidin sorption are studied by varying initial solution pH, initial concentration, adsorbent dose and temperature. Kinetically, the melanoidin removal from solution by a surfactant modified zeolite is rapid and the amount adsorbed is dependent on pH, initial concentration, adsorbent dose and temperature. The equilibrium sorption data are fitted to the Freundlich and Langmuir models while the sorption kinetics are described by the Ho pseudo-second order and Elovich models. The thermodynamic analysis indicates that the sorption is spontaneous and endothermic in nature. The FTIR spectra analyses show no new peaks or shift in peaks after sorption indicating that the melanoidin sorption may have occurred by a physical process. The results from desorption studies showed that melanoidin eluted back easily to the solution using distilled water which corroborates the physical sorption mechanism.

Key words: melanoidin; surfactant modified zeolite; sorption; equilibrium; kinetics.

Melanoidin is an antioxidant that results from the Malliard reaction found in fermentation and distillation processes [1]. Industries that use molasses as a major source of carbon in their fermentation processes like in the ethanol production, bakery yeast processing and brewery produce effluents that contain melanoidin. Effluents from these industries and especially the distillery have a dark brown color [2]. If such effluents are discharged into receiving water bodies such as rivers and streams, the color impacts negatively on light penetration. The consequence is reduced availability of light to the biota and hence reducing oxygenation of the water by photosynthesis. Also, public perception of water quality is influenced by color, i.e., the presence of unnatural colors is aesthetically unpleasant [3]. Consequently, melanoidin must be removed from industrial effluents before discharge.

Several conventional techniques have been employed to remove melanoidin from distillery wastewater including biological, physico-chemical, electrochemical and membrane technologies. Among these techniques, biological processes are the most common. For instance, the use of activated sludge treatment, the use of fungi such as Coriolus, Aspergillus, Phanerochaete and certain bacterial species such as Bacillus, Alcaligenes and Lactobacillus has been explored [4-7]. However, these methods are insufficient to treat the wastewater released from distilleries because melanoidin has antioxidant properties and is therefore toxic to many organisms typically used in wastewater treatment processes [8]. To enhance melanoidin removal after a biological process, it is imperative to have a polishing stage incorporated in the wastewater treatment train. The use of adsorption could be the best post-treatment option [8].

The use of adsorption in water and wastewater treatment inheres in its simplicity, low-cost of operation and wide end-use applications [9]. The starting point in any adsorption based technology is the choice of appropriate media [10]. A number of media have been tested in the removal of melanoidin from distillery wastewater. These include commercial activated carbon (CAC), cane bagasse activated carbon,

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bottom bagasse ash-activated carbon (BBA-AC) and coal fly ash activated carbon (CFA-AC) [8,11-14]. This family of activated carbons has shown appreciable decolorization and melanoidin removal rates. The use of activated carbons in the removal of melanoidin from distilleries or molasses spent wash may be restricted owing to the high cost of the material and/or the dependence of performance on the activated carbon type [15-16]. There is therefore a need to conduct intensive research to develop materials that are robust, cheap and effective in decolorization of distillery wastewater.

In order to develop effective sorption materials for the removal of melanoidin from aqueous solution, it is essential to understand the sorption behaviour of melanoidins. Ikan *et al.* [17] reported that the sorption behaviour of melanoidin depended primarily on sugar-derived backbone of the melanoidin structure. Cosovic *et al.* [18] also reported that melanoidins that were prepared from glucose only as well as those prepared from glucose and amino acids exhibited the same sorption behaviour and thus concurring with other research studies reported by Cammerer *et al.* [19-20]. Studies have shown that chemical composition, molecular mass, hydrophobicity and sorption properties of synthetic melanoidin depend on the reacting components and reaction time. There is a general increase in the proportion of hydrophobic components within melanoidins as the reaction times are increased during melanoidin preparation. Hydrophobic properties of organic molecules have been shown to significantly influence their sorption onto mineral particles [21-22]. Because of the existence of different formulations of melanoidins and their different sorption behavior, this study considered the procedure reported by Bernardo *et al.* [14] in the preparation of melanoidin and explored its uptake by modified zeolite.

Zeolite has been reported as one of the emerging mineral particles (adsorbent) used in water and wastewater treatment due to its ability to adsorb a wide range of contaminants like organics, inorganic cations and anions [23-27]. Owing to its net negative charge natural zeolite usually have little or no affinity for anions and also exhibits very low adsorption for organic molecules. As such, several studies have reported the use of organic surfactants to reverse the surface charge on zeolite. Majdan *et al.* [28] modified chabazite with hexadecyltrimethylammonium bromide (HDTMABr) for chromate removal while Benkli *et al.* [29] modified organozeolite surface for the removal of reactive azo dyes. Ersoy and Celik [30] investigated the adsorption of aniline and nitrobenzene on natural zeolite and HDTMA-modified zeolite (SMZ) and re-

ported that the adsorption capacity of aniline and nitrobenzene onto natural zeolite surface was very low but was significantly high on SMZ. It can be concluded that the alteration of the surface properties of zeolite through chemical modification creates new adsorption sites that have affinity for targeted ions in solution. In this study, we explore the use of functionalized natural zeolite as an adsorbent for the sorption of melanoidin. Natural zeolites are relatively cheap and are abundantly available in South Africa where they can find application in polishing wastewater from local distilleries. The functionalization was done according to a procedure reported elsewhere in which the raw zeolite was pretreated with cationic surfactant: HDTMA-Br [23]. Batch experiments were then conducted to explore the melanoidin sorption features of the functionalized zeolite under different process conditions such as sorbent mass, initial melanoidin concentration, initial pH of solution and temperature. Equilibrium data are described by the Langmuir and Freundlich isotherm models while the Ho pseudo-second order and Elovich models are used to fit kinetic data. The thermodynamic behavior of melanoidin sorption is discussed.

MATERIALS AND METHODS

Preparation of synthetic melanoidin

Synthetic melanoidin was prepared using the procedure presented by Bernardo *et al.* [14]. Accordingly, it involved mixing 4.5 g of glucose (G8270 D--(+), Sigma-Aldrich), 1.88 g of glycine (G7126, reagent plus TM ≥ 99%, Sigma-Aldrich) and 0.42 g of sodium bicarbonate with 100 mL of distilled water and then heating for 7 h at 95 °C. After heating, 100 ml of water was added. The prepared solution had an initial concentration of 29650 mg/L from which dilute solutions were prepared. The solution pH was adjusted by 0.1 M NaOH and 0.1 M NaCl to a value of 6.5.

Surface modification of zeolite

The natural zeolite (clinoptilolite, Si/Al = 5.2) was purchased from Jax Industries, South Africa while the synthetic F9 zeolite (X-type, Na-form, Si/Al = = 1.23) was purchased from Wako Chemicals, Japan. The procedure for surfactant modification was reported by Onyango *et al.* [23]. Accordingly, the natural zeolite was first transformed to a near homoionic state. This involved thoroughly washing the raw natural zeolite with deionised water to remove dirt then allowing it to air dry for 24 h. A sample of 20 g of the dried natural zeolite was then added to 2 M NaCl solution at room temperature. The mixture was placed in a batch reactor and stirred at 200 rpm for 3 days

after which it was vacuum filtered. This was followed with washing with deionised water to remove excess NaCl then allowing the zeolite to air dry for 12 h.

Functionalization of both natural and synthetic zeolites involved the use of hexadecyltrimethyl ammonium bromide (HDTMA-Br) (Sigma Aldrich, South Africa). Pre-weighed quantities of the zeolites were separately treated with 3 g/L HDTMA-Br solutions in 1:100 (solid:liquid) on a w/v ratio. The mixture was placed in a batch reactor for 3 days at a constant stirring speed of 200 rpm. Finally, the mixture was vacuum filtered and the solid residue (surfactant modified zeolite) double washed with deionised water and then air dried for subsequent use in characterization and sorption experiments.

Characterization of the zeolite materials

The natural clinoptilolite, Na-form and surface modified forms of zeolite materials were characterized using the Fourier transform infrared spectroscopy (FTIR) and point-of-zero charge. The FTIR analysis was carried out using Perkin Elmer Spectrum 100 spectrometer. The spectra were recorded in the region from 500 to 4000 cm^{-1} with a spectra resolution of 4 cm^{-1}. To determine the point of zero charge (pH$_{pzc}$), batch equilibrium technique was used [31]. This involved contacting 40 mL deionised water samples at pH 2-12 with 0.5 g of the Na- and modified forms of the zeolites. The sample bottles were placed in a thermostatic shaker operated at 200 rpm for 24 h. Thereafter, the samples pH values (final pH) were recorded and the difference between the initial and final pH noted. A plot of drift in pH (final pH minus initial pH) *vs.* initial pH was used to determine the pH$_{pzc}$.

Batch experiments

Sorption equilibrium

In the first set of experiments, the effect of adsorbent mass using surfactant modified natural and synthetic zeolites was investigated. Pre-weighed amounts of the adsorbents ranging from 0.1 to 3.5 g were contacted with 40 mL melanoidin solutions of initial concentration of 5930 mg/L contained in plastic sample bottles. The bottles were placed in a thermostatic shaker operated at 200 rpm for 24 h. At the end of the experiment, the samples were removed from the shaker, filtered using a Whatman Filter Paper No. 42 and the filtrate analyzed for residual melanoidin concentration using a UV-Visible spectrophotometer (Pharmacia Biotech Ultraspec 3000) at a wavelength of 475 nm. In the subsequent set of experiments the effect of initial concentration, initial pH of solution and temperature were investigated at fixed surfactant modified natural zeolite (SMZ) sorbent mass of 0.5 g and

40 mL melanoidin solution. The effect of the initial concentration was explored by varying the concentration from 1482.5 to 15575 mg/L. For the effect of pH, the experiment was carried out by varying the initial solution pH from 2 to 12 using either NaOH (0.1 M) or HCl (0.1 M). Sorption isotherm study was carried out using fixed melanoidin initial concentration and pH at 5930 mg/L and 6.5, respectively, at varied temperatures of 25, 35 and 45 °C. The experimental procedure and melanoidin analysis were similar to those described under the effect of sorbent mass.

The percentage color removal or decolorization efficiency (R_t) was calculated using the formula:

$$R_t = 100 \frac{Abs_0 - Abs_f}{Abs_0} \tag{1}$$

where Abs_0 is the initial absorbance and Abs_f is the final absorbance of the melanoidin solution. Melanoidin equilibrium sorption capacity was calculated by:

$$q_e = \left(\frac{c_0 - c_e}{m} \right) V \tag{2}$$

where q_e is the melanoidin uptake at equilibrium (mg/g), c_0 and c_e are the initial and final concentrations (mg/L), respectively; V is the volume of melanoidin solution (L) and m is the sorbent mass (g).

Sorption kinetics

Kinetic experiments were carried out using a 1 L batch reactor operated at a stirring speed of 400 rpm. The initial melanoidin concentration was varied from 1482.5 to 8895 mg/L. The adsorbent mass was fixed at 10 g while the temperature at 25 °C. To generate kinetic data, at time zero and at predetermined time intervals thereafter, 5 mL samples were withdrawn from the reactor using a 10 mL syringe. The samples were filtered through a Whatman filter paper No. 42 filter paper. The filtrates were then analysed for melanoidin concentration using UV-Visible spectrophotometer (the Pharmacia Biotech Ultraspec 3000) at a wavelength of 475 nm. The amount of melanoidin sorbed was calculated using Eq. (3):

$$q_t = \left(\frac{c_0 - c_t}{m} \right) V \tag{3}$$

where q_t is the time-dependent amount of melanoidin sorbed per unit mass of adsorbent (mg/g) and c_t is the bulk-phase melanoidin concentration at any time (mg/L).

Desorption studies

Desorption experiments were done to further examine the mechanism of melanoidin sorption. Following reaction to remove melanoidin from solution, the SMZ adsorbent was separated from solution and

re-suspended for 24 h in distilled water. After contact, a sample was taken and filtered through a Whatman filter paper No. 42 filter paper. The filtrate was then analysed for melanoidin concentration using UV-Visible spectrophotometer.

RESULTS AND DISCUSION

Characterization of the zeolite materials

The FT-IR spectra of the raw clinoptilolite, Na--form and the modified form, are shown in Figure 1. The characteristic (spectra) bands at 1000-950 cm^{-1} are due to Si-O-Si and Si-O-Al vibrations, the presence of zeolitic water (3600, 3450 and 1640 cm^{-1}) and pseudo-lattice vibrations (800-500 cm^{-1}). The spectra of the surfactant-modified zeolites (Figure 1) have two additional sharp bands in the region 3000-2800 cm^{-1} assigned to the asymmetric and symmetric stretching of the C-CH$_2$ group of the alkyl chain. The point-of-zero charge (pH$_{pzc}$) of the surfactant modified natural zeolite was found to be 8.0.

Effect of adsorbent mass on melanoidin decolorization efficiency

In the first set of sorption experiments, the decolorization of synthetic wastewater containing melanoidin at a concentration of 5930 mg/L was explored.

Figure 2 shows the effect of varying adsorbent mass for the different forms of zeolite: raw natural zeolite, modified forms of synthetic (F9) and natural (clinoptilolite) on the decolorization efficiency. Results in Figure 2 indicate that while on the one hand raw natural zeolite had almost zero sorption for melanoidin, on the other hand the surfactant-modified zeolites (SMZs) showed enhanced sorption capacities. The increased sorption by SMZs is attributed to the loaded HDTMA. This observation concurs well with the findings of previous work that has shown that surface modification enhances the sorption of organic pollutants onto SMZ [32-35]. The percentage melanoidin removal expressed as decolorization efficiency increased with an increase in the adsorbent dose for the modified forms of the zeolites. This observation is due to the fact that active sites available for melanoidin sorption are proportional to the adsorbent mass. Interestingly, the modified natural zeolite performs better than the modified F9 (low silica zeolite). This phenomenon requires further investigation to explore the roles of impurities in the natural zeolite and other zeolite properties such as hydrophobicity (increases with an increase in silica to alumina ratio) in the removal of melanoidin from aqueous solution.

Overall, the decolorization efficiencies (up to 87%) achieved in this study are significant and compare
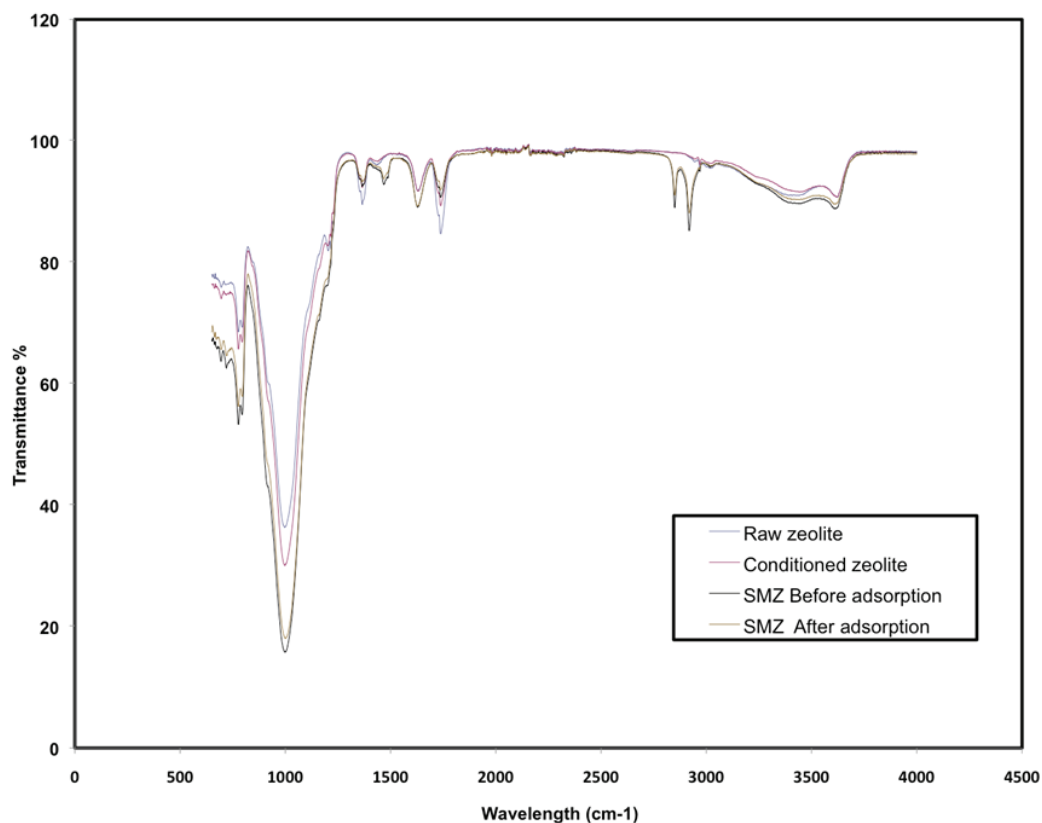

Figure 1. FTIR Spectra of raw, conditioned and surfactant modified zeolite (SMZ) before and after adsorption of melanoidin.
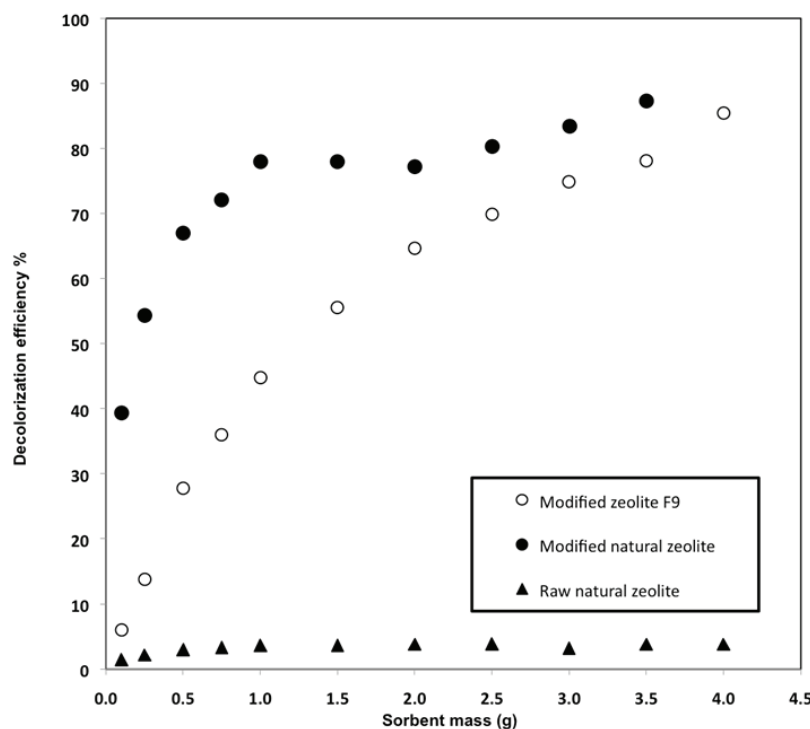
Figure 2. Decolorization performances of raw and surfactant modified natural and synthetic zeolites
(initial concentration: 5930 mg/L, pH 6.5, temperature: 298 K, particle size: 0.15-0.30 mm).

favorably well with those of other adsorbents reported in literature. For instance, Simaratanamongkol and Thiravetyan obtained 97.75 and 4.10% decolorization efficiencies using bottom bagasse ash activated carbon and commercial activated carbon, respectively, from a solution containing 100 mg/L melanoidin [36].

Effect of initial concentration

Concentration of melanoidin in the target wastewater may vary from one industry to another. Using surfactant modified natural zeolite (SMZ), decolorization efficiency (expressed in %) and melanoidin uptake (expressed in mg/g) were explored for a change in the initial concentration. Increasing the initial melanoidin concentration resulted into a corresponding reduction in the decolorization as shown in Figure 3. Specifically, the decolorization decreased from 77 to 49% when the initial concentration was increased from 1482.5 to 15575 mg/L. However, the sorption capacity increased from 92 mg/g to 611 mg/g for the same increase in initial concentration. The results on the sorption capacity imply that at low concentration, only a few active sites on the adsorbent are occupied while at higher concentration a larger fraction of the active sites become occupied with melanoidin.

Effect of initial solution pH

Figure 4 shows the effect of pH on decolorization and melanoidin uptake. In the pH range of 2-5,
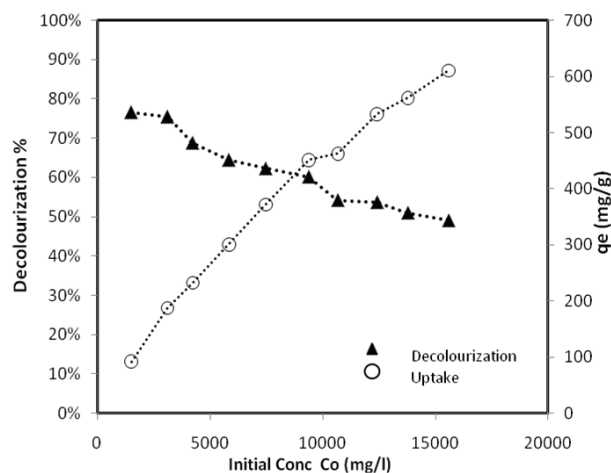

Figure 3. Effect of initial concentration on the performance of SMZ (sorbent mass: 0.5 g, pH 6.5, temperature: 298 K, particle size: 0.15-0.30 mm).

there is a steep increase in the decolorization and uptake while a gradual increase is observed in the pH range 5-12. These observations could be explained in terms of adsorbate and adsorbent properties. At low pH (1.0-2.5) melanoidin has a net positive charge. The surface of the adsorbent is also positively charged because the pH_{pzc} of SMZ is 8.0. This results in a very low melanoidin removal from solution because of coulombic repulsive forces. Because the chemical properties of melanoidins resemble humic substances,
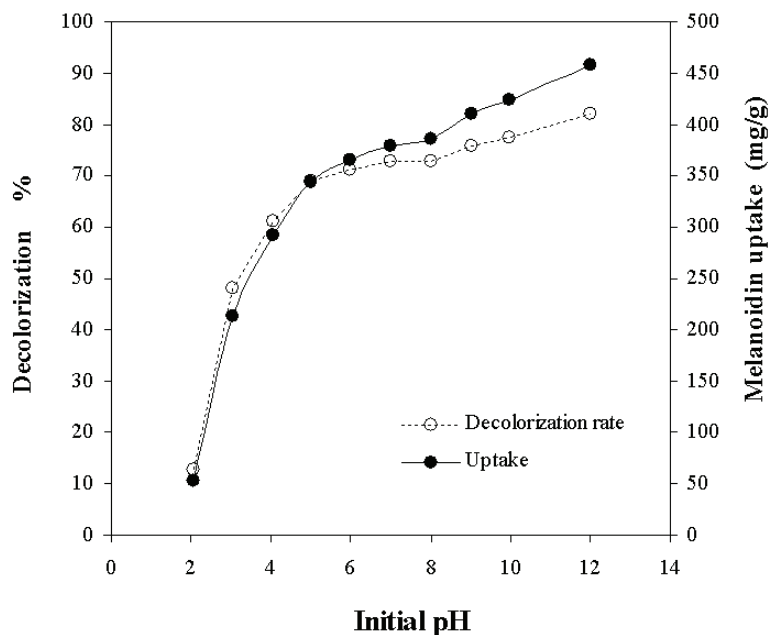
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Figure 4. Effect of pH on decolorization and sorption uptake (temperature: 298 K; Initial concentration: 5930 mg/L; sorbent mass: 0.5 g, particle size 0.15-0.30 mm, initial system pH 6.5).

i.e., acidic, polymeric and highly dispersed colloids, they are negatively charged at pH > 2.5 due to the dissociation of carboxylic and phenolic groups [37--38]. Thus attractive interaction between the positively charged adsorbent (SMZ) and negatively charged adsorbate (melanoidin) occurred resulting in increased decolorization and uptake with an increase in pH. Interestingly, the decolorization and uptake increase above the pH_{pzc} of the SMZ. Beyond pH_{pzc} SMZ surface charge is reversed and becomes negative. However, there is still continued decolorization and melanoidin uptake. This phenomenon suggests that multiple mechanisms could be involved in the sorption of melanoidin onto SMZ. Hydrophobic interaction and hydrogen bonding are suggested to be the major mechanism in organic sorption by SMZ [30,35,39]. A large number of hydrogen bonds between C or N of HDTMA and hydroxyl groups, carboxylic groups and phenolic groups of melanoidin could additionally guarantee the effective sorption of melanoidin [19,28,32].

Effect of temperature

The influence of temperature on melanoidin sorption was explored by varying temperature in the range of 25-45 °C. Results are shown in Figure 5 in which the adsorption capacity increases with an increase in temperature, indicating that melanoidin sorption on SMZ is endothermic in nature. The enhanced sorption at higher temperature may arise from a decrease in the thickness of the boundary layer surrounding the adsorbent. In addition, there is a possibility of an increase in the mobility of the solute molecules with a

rise in temperature [40]. Both phenomena enhance mass transfer of adsorbate.
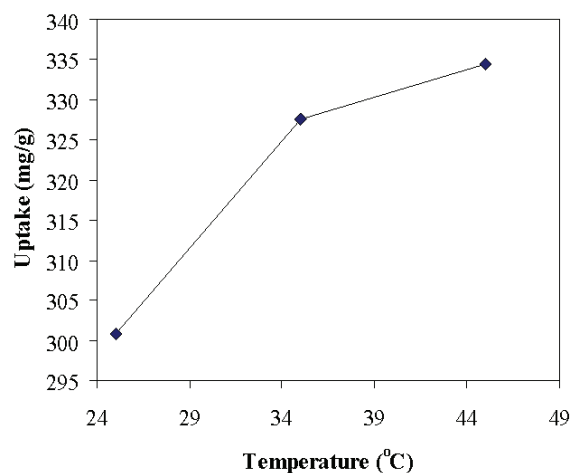

Figure 5. Melanoidin equilibrium sorption capacity as a function of temperature (5930 mg/L; sorbent mass: 0.5 g; particle size: 0.15-0.30 mm).

Sorption isotherm

Sorption equilibrium data provides crucial information that is useful in understanding adsorbate-adsorbent interaction and for effective design of an adsorption process. Moreover, sorption equilibrium data are used in comparing the performance of different media for a given sorption process. The sorption isotherms of melanoidin removal by SMZ at temperatures of 25, 35 and 45 °C are shown in Figure 6. An increase in equilibrium concentration results in a cor-

responding increase in equilibrium uptake. Also, it is observed that an increase in temperature results in an increase in the uptake of melanoidin, which confirms the endothermic nature of the present sorption system. The experimental data were further analysed by the two extensively used isotherm models viz. Langmuir and Freundlich models [41-42]. The Langmuir and Freundlich isotherm parameters are given in Table 1. From the Langmuir isotherm, the maximum adsorption capacity (q_m) increases from 823.7 to 1157.0 mg/g as the temperature is increased from 25 to 45 °C. The q_m values compare favorably with those reported in literature (Table 2). The predicted K_F values from the Freundlich isotherm decrease with an increase in temperature. Since K_F is related to sorption capacity, the observation contradicts the results presented in Figure 5, which suggest that sorption in enhanced at higher temperature. Thus, the Freundlich model is not be a good representation of the present sorption system.
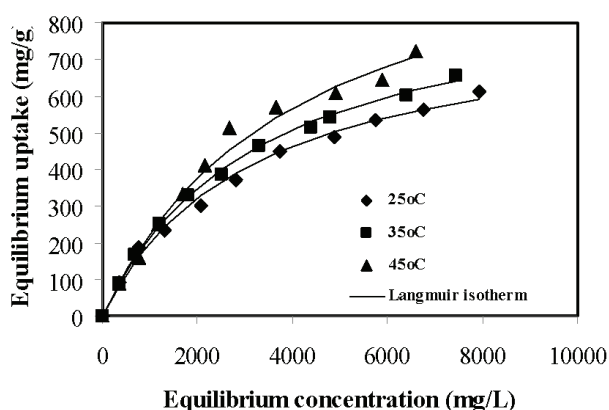

Figure 6. Adsorption isotherms for melanoidin sorption on SMZ (sorbent mass: 0.5 g; temperature: 298 K, particle size: 0.15-0.30 mm).

Thermodynamic studies

The thermodynamic parameters such as changes in entropy ($\Delta S°$), enthalpy ($\Delta H°$) and standard Gibbs free energy ($\Delta G°$) for the sorption of melanoidin by the SMZ were determined using the following equations:

$$\ln\left(\frac{mq_e}{c_e}\right) = \frac{\Delta S°}{R} + \frac{-\Delta H°}{RT} \qquad (4)$$

$$\Delta G° = -RT \ln\left(\frac{mq_e}{c_e}\right) \qquad (5)$$

where m is the sorbent dose (g/L), R (kJ mol^{-1} K^{-1}) is the gas constant and T is the temperature in K. The ratio mq_e/c_e is referred to as adsorption affinity. A plot of ln (mq_e/c_e) versus $1/T$ according to Eq. (4) is shown in Figure 7. From the plot, both the change in entropy ($\Delta S°$) and the enthalpy ($\Delta H°$) of sorption were determined and are 67.28 J mol^{-1} K^{-1} and 19.67 kJ/mol, respectively. The positive value of $\Delta H°$ is consistent with the endothermic nature of the sorption process while the positive value of $\Delta S°$ suggests an increase in disorder at the solid-liquid interface. From Eq. (5) the values of change in standard Gibbs energy were computed and found to be -0.42, -0.96 and -1.77 kJ/mol for 25, 35 and 45 °C, respectively. The decrease in $\Delta G°$ values with an increase in temperature indicates the spontaneous nature of the adsorption process.

Sorption kinetics

For practical applications of sorption such as process design and control, it is important to model the sorption rate and to establish the time dependence of sorption systems under various process conditions [43]. Consequently, the kinetic behaviour of melanoidin sorption onto SMZ was examined by varying the initial concentration as shown in Figure 8. It can be seen that the rate of sorption of melanoidin was quite rapid in the first 20 min and gradually slowed down in the remaining sorption period. Such two-stage phenomenon is quite common in many sorption systems [44-46]. The initial rapid rate (stage 1) may be attributed to the availability of unoccupied sites on the sorbent and the high driving force for sorption, which is the initial concentration gradient between the bulk phase and the adsorbent phase. As sorption progresses, the driving force is attenuated and this leads to a slower uptake rate (stage 2). From Figure 7, it can be seen further that the melanoidin uptake increased with an increase in initial concentration. The higher the initial concentration the higher is the driving force leading to an increased melanoidin uptake.

To mathematically describe the kinetics of the present sorption process, the Ho pseudo-second or-

Table 1. Langmuir and Freundlich isotherm parameters for melanoidin sorption onto SMZ

Temperature, °C	Langmuir constants			Freundlich constants		
	q_m / mg g^{-1}	b / 10^{-4} L mg^{-1}	R^2	K_F	$1/n$	R^2
25	823.7	3.2	0.98	3.45	0.58	0.98
35	918.9	3.1	0.99	2.62	0.63	0.98
45	1157.0	2.4	0.96	1.50	0.72	0.97

Table 2. Comparison of adsorption capacity of the SMZ with other adsorbents for melanoidin removal from aqueous solution

Adsorbent	q_m / mg g^{-1}	Reference
Surfactant modified zeolite	823.7-1157.0	This study
Activated carbon obtainedfrom bagasse bottom ash	200.0-232.6	[12]
Activated carbonfrom bagasse (Thailand)	1720	[14]
Activated carbonfrom bagasse (Brazil)	2450	[14]
Phosphoric acidtreated bagasse	96.2	[50]
Steam treated commercial activated carbon	666.7	[50]
Activated carbon	555.6	[50]
Chitin nanofibre	242	[51]
Chitosan	99	[51]
Chitin	61	[51]
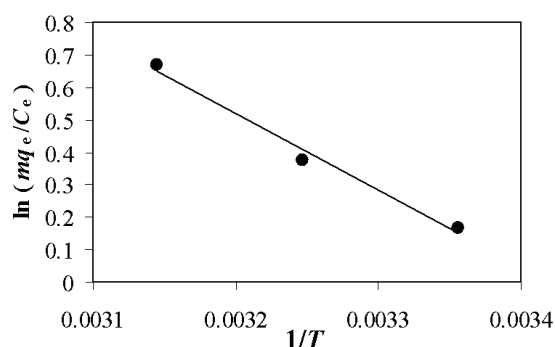
Figure 7. Plot of ln (mq$_e$/c$_e$) versus 1/T for melanoidin sorption to determine thermodynamic parameters.

der and Elovich kinetic models were used to fit the kinetic data. The linearized form of the pseudo-second-order equation given by [46]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (6)$$

where k_2 (g mg^{-1} min^{-1}) is the pseudo-second order rate constant and all other parameters are as defined earlier. From the pseudo-second order kinetic model, the initial sorption rate, h_0 (mg g^{-1} min^{-1}) can be defined as:

$$h_0 = k_2 q_e^2 (t \rightarrow 0) \qquad (7)$$

A summary of the pseudo-second order kinetic parameters are given in Table 3. On one hand, the calculated q_e and h_0 values show a general increase with an increase in the initial concentration. On the other hand, the rate constant k_2 values decrease with an increase with initial concentration. The deviation in the trend of h_0 and k_2 at a concentration of 2965.0 mg/L is not clear.

The linear form of the Elovich equation is given by [50]:
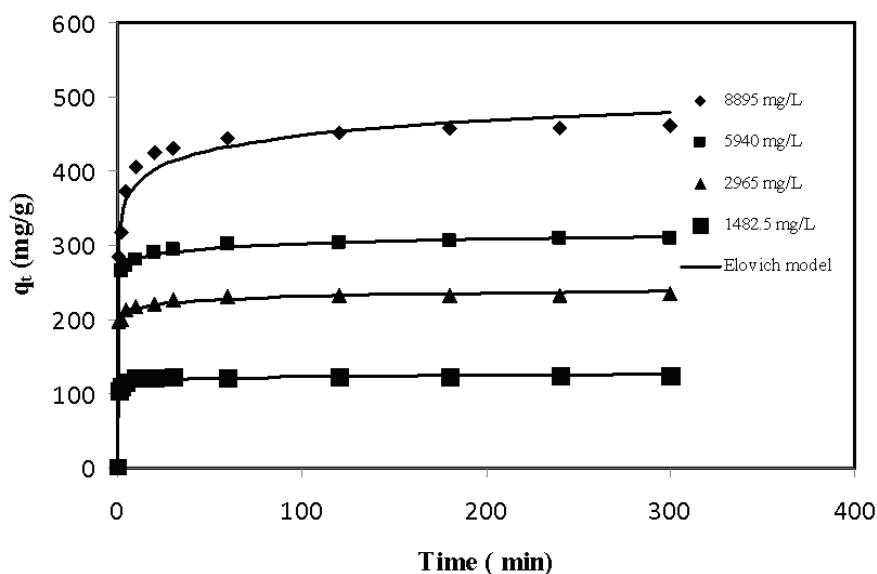
$$q_t = \frac{1}{b}\ln t + \frac{1}{b}\ln(ab) \qquad (8)$$

Figure 8. Kinetic study of melanoidin adsorption on SMZ (temperature: 298 K, pH 6.5, sorbent dose: 10g/L, particle size: 0.15-0.30 mm).

where a (mg g^{-1} min^{-1}) and b (g/mg) are Elovich parameters related to initial sorption rate and surface coverage, respectively. The Elovich parameters were determined and are summarized in Table 3. The predicted initial rate of sorption is extremely large and increases with an increase in the initial concentration due to enhanced driving force at higher concentration. Such large values have been reported for sorption of phenol on HDTMA-zeolite (a = 3.28×10^9 mg g^{-1} min^{-1}), phenol on pinewood activated carbon (a = 4.4×10^{18} mg g^{-1} min^{-1}) and AB264 on pinewood activated carbon (a = 3.6×10^8 mg g^{-1} min^{-1}) [47]. The parameter related to surface coverage, b, decreases with an increase in the initial concentration. This is due to the fact that at higher concentration, more active sites are consumed.

To compare both the pseudo-second order model and Elovich model on equal basis, standard deviation (S.D.) between experimental data and model prediction was used. The S.D. is defined as:

$$S.D.(\%) = 100 \frac{\sum_{N}\left(1 - q_{t,cal}/q_{t,exp}\right)^2}{N} \qquad (9)$$

where $q_{t,exp}$ and $q_{t,cal}$ are the experimental and calculated q_t values, respectively, and N is the number of data points. Table 4 gives a summary of S.D. values

Mechanism of melanoidin sorption onto surfactant modified zeolite

The sorption mechanism was studied by considering desorption of melanoidin from used SMZ and exploring the FTIR spectra before and after melanoidin sorption. From the desorption studies, melanoidin was easily eluted back to solution using distilled water suggesting that melanoidin was weakly bound on SMZ. From the FTIR spectra shown in Figure 1 it is observed that there are no new peaks or shift in peaks after melanoidin sorption on SMZ. This similarity in the peaks before and after sorption suggests that the sorption process may have been due to physical mechanism. Studies conducted by Migo *et al.* [38] show that melanoidin has a net negative charge at pH values > 2.5. The SMZ used in this study has a net positive charge up to a pH value of 8.0. Within this pH range of 2.5 to 8.0 the attractive interaction between the positively charged adsorbent (SMZ) and negatively charged adsorbate (melanoidin) is responsible for the sorption, which is physical in nature.

Regeneration of used SMZ was not considered. Given the low cost nature of natural zeolite, it is proposed to use the SMZ as a single-use sorbent as regeneration may unnecessarily be high in cost. Since both natural zeolites and distillery waste effluents are

Table 3. Summary of kinetic parameters for melanoidin sorption onto SMZ

Initial concentration, mg/L	Pseudo second order parameters				Elovich parameters		
	$q_{e,cal}$ / mg g^{-1}	h_0 / mg g^{-1} min^{-1}	k_2 / 10^{-3}g mg^{-1} min^{-1}	R^2	a / mg g^{-1} min^{-1}	b / g mg^{-1}	R^2
1482.5	125	200	12.8	1.000	1.48×10^6	0.312	0.793
2965.0	250	333	53.3	1.000	1.48×10^{14}	0.151	0.955
5940.0	333	250	2.2	1.000	3.99×10^{14}	0.112	0.976
8895.0	500	333	1.3	0.999	1.49×10^{16}	0.034	0.903

Table 4. Predicted pseudo second order and Elovich equations for melanoidin adsorption onto surfactant modified zeolite

c_0 / mg l^{-1}	Pseudo second order equation		Elovich equation	
	q_t / mg g^{-1}	S.D., %	q_t / mg g^{-1}	S.D., %
1482.5	200t/ (1 + 1.60t)	8.67	3.200 ln t + 108.4	2.66
2965.0	333t/ (1 + 1.33t)	10.83	6.614 ln t + 200.1	1.23
5930.0	250t/ (1 + 0.75t)	9.93	8.919 ln t + 261.0	0.72
8895.0	333t/ (1 + 0.67t)	12.02	28.98 ln t + 314.3	4.86

for both the pseudo second order and Elovich models, together with predicted equations. From the relatively lower S.D. values obtained from the Elovich model, the present sorption system is better described by the Elovich kinetic model.

used in agriculture [48-49], a prudent way to dispose used SMZ is to apply it in farming.

CONCLUSIONS

Surfactant modified zeolite was prepared and it was demonstrated that the media is effective for melanoidin removal from water. The sorption process

was physical in nature and found to be affected by sorbent dose, pH, initial concentration and temperature. From the kinetics point of view, melanoidin sorption was rapid and described by the Elovich equation. The equilibrium uptake followed the Freundlich and Langmuir isotherms. The Langmuir maximum sorption capacity ranged from 823.7 to 1157.0 mg/g, which is competitive relative to other materials reported in literature. Given the low cost nature of natural zeolite, it is possible to apply the sorbent in polishing distillery wastewater after a biological process. To be successful in this endeavour, further research is still required to obtain more data for system design.

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NAUČNI RAD

SORPCIJA MELANOIDINA NA POVRŠINSKI MODIFIKOVANOM ZEOLITU

Melanoidin je odgovoran za tamno braon boju otpadne vode destilerija. Ispuštanje obojene otpadne vode ima glavni ekološki uticaj na biotu vode kojs je prima. Ova studija istražuje izdvajanje melanoidina iz vodenog rastvora. Ravnoteža, kinetika i termodinamika sorpcije melanoidina su proučavane pri različitim početnim pH i koncentracijama rastvora i količina adsorbenta, kao i temperaturama. Izdvajanje melanoidina iz rastvora površinski modifikovanim zeolitom je brzo, a adsorbovana količina zavisi od pH, početne koncentracije, doze adsorbensa i temperature. Freundlich-ov i Langmuir-ov model fituju ravnotežne podatke, a Ho-ov model pseudo-drugog reda i Elovich model - kinetičke podatke. Tremodinamička analiza ukazuje da je sorpcija spontana i endotermna po svojoj prirodi. FTIR spektri ne pokazuju nove pikove posle sorpcije, što ukazuje da se sorpcija melanoidina odigrava kao fizički process. Rezultati proučavanja desorpcije su pokazali da se melanoidin lako eluira destilovanom vodom, što potvrđuje mehanizam fizičke sorpcije.

Ključne reči: melanoidin, površinski modifikovani zeolit, sorpcija, ravnoteža, kinetika.