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Bada, S.O. and Potgieter-Vermaak, S., 2008. Evaluation and treatment of coal fly ash for adsorption application. Leonardo Electronic Journal of Practices and Technologies, 12, pp.37-48.

Experimental study and dynamic simulation of melanoidin adsorption from distillery effluent

Shoaib AQ1 Ahmed, 1✉,2

Email shoaib.quershi@duet.edu.pk

Imran Nazir Unar, 3

Hassnain Abas Khan, 4

Ghulamullah Maitlo, 2

Rasool Bux Mahar, 1

Abdul Sattar Jatoi, ²

Abdul Qayoom Memon, ²

Abdul Karim Shah, ²

¹ U.S.-Pakistan Center for Advanced Studies in Water, Mehran University of Engineering and Technology AQ2, Jamshoro, Sindh, 76060 Pakistan

² Chemical Engineering Department, Dawood University of Engineering and Technology, Karachi, Sindh, 74800 Pakistan

³ Chemical Engineering Department, Mehran University of Engineering and Technology, Jamshoro, Sindh, Pakistan

⁴ Clean Combustion Research Center, Division of Physical Sciences and Engineering, King Abdullah University of Science and Technology (KAUST), Thuwal, 23955-6900 Saudi Arabia

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Abstract

This work aims to utilize fly ash from a thermal power station for melanoidin reduction from distillery effluent by adsorption. To accomplish this, coal fly ash was modified through chemical treatment and was then tested for melanoidin adsorption as a function of various melanoidin concentrations, contact time, and pH. The specific novelty of this study is the evaluation of coal fly ash as a low-cost adsorbent for melanoidin removal. Furthermore, the simulation study was carried out using Aspen ADSIM software in order to optimize the commercial usage of the prepared adsorbent. The main results achieved include the maximum removal efficiency of 84% which was reached at initial melanoidin concentration of 1100 mg L⁻¹ (5% dilution), pH 6, and a contact time of 120 min. The Langmuir and Freundlich isotherm models were used to evaluate adsorption isotherms. The maximum adsorption capacity of 281.34 mg/g was observed using the Langmuir isotherm. Furthermore, pseudo-first- and pseudo-second-order and intra-particle diffusion models were used to fit adsorption kinetic data. The pseudo-second-order was best describing the adsorption kinetic with a faster kinetic rate of 0.142 mg g⁻¹ min⁻¹. CFA (coal fly ash) after acidic activation

resulted in a slightly higher surface area, average pore volume, and pore size. The maximum breakthrough time and adsorbent saturation time were achieved at initial melanoidin concentration of 1 mol/lit, bed height of 2.5 m, and flow rate of 50 lit/min.

Keywords

Melanoidins
Fly ash
Adsorption
Isotherms
Kinetics
Aspen Adsim
Simulation

Highlights

- Strong acid-treated fly ash adsorbent is presented for melanoidin uptake.
- Langmuir isotherm and pseudo-second-order kinetic model describe the melanoidin adsorption.
- The dynamic column performance is modeled in Aspen Adsim[®] simulation software.
- Developed model is presented for breakthrough curves of different process conditions.
- Treated fly ash adsorbent is excellent for melanoidin uptake from real distillery effluent.

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Introduction

Melanoidins are intense dark brown complex organic polymers produced in the last stage of the Millard reaction; it is a non-enzymatic reaction between carbohydrate and amino groups of reduced sugar (Liakos and Lazaridis 2016). They are present in food items, such as coffee, honey, and beer, having physiological characteristics of antimicrobial, antioxidant, and antihypertensive activity (Arimi et al. 2014; Kaushik et al. 2017). Melanoidins are a significant component (nearly 2%) of

effluent (spent wash) produced in molasses-based ethanol distilleries (Martins and Boekel 2005; Tiwari et al. 2013). Owing to their characteristics and structural complexity, they are difficult to be removed by conventional anaerobic-aerobic digestion methods. For instance, they are intensified in anaerobic treatment and once they are disposed of, they begin to cause several issues (Arimi et al. 2014). Spent wash, when it is released in freshwater, decreases sunlight penetration, which ultimately leads to a decline in the concentration of dissolved oxygen and photosynthesis is retarded, as well (Liang et al. 2009). Hence, the removal of melanoidins from wastewater provides a possible and necessary resolution for distillery effluent treatment. Different organic, inorganic, and biological contaminants are found in wastewater (Arica et al. 2019) and various methods such as chemical, physical, and biological are applied for removal of pollutants from wastewater (Arica et al. 2017). Biosorbents prepared for purification are simple, low-cost, flexible, and energy-saving and have high uptake pollutant efficiency (Elgarahy et al. 2019). Dye from the aqueous solution is captured using chitosan as an adsorbent material due to its easy availability and low investment cost (Elwakeel et al. 2016b). Glycidyl methacrylate (GMA) is also used as an adsorbent due to its larger pore size, low toxicity, and lower cost (Elwakeel et al. 2016a).

Furthermore, various approaches have been applied to the reduction of melanoidins from anaerobically treated effluent, which includes adsorption on activated carbon (Satyawali and Balakrishnan 2008), Fenton's oxidation (Liang et al. 2009), nanofiltration and reverse osmosis (Singh et al. 2018), and electrochemical oxidation using various electrolytes (Susree et al. 2013). Apart from these physicochemical treatment methods, biological treatment by various microorganisms has also been studied, such as aerobic treatment using white-rot fungi (Dahiya et al. 2001; Raghukumar et al. 2004). These technologies, however, have some drawbacks such as high operating and equipment cost, they are less efficient for color removal, and sometimes they generate a huge amount of hazardous by-products (Arimi et al. 2015; Chandra et al. 2008).

Among all the technologies, sorption on activated carbon was found the most efficient for color and organic pollutant removal from the aqueous and industrial effluent. However, activated carbon is expensive and has not been adopted widely (Krishna Prasad and Srivastava 2009b). Therefore, it can be substituted with any less-expensive materials. Previously, a number of waste-based, low-cost activated carbon substances have been developed and investigated for use in the uptake of melanoidins and were found nearly equally efficient as commercial activated carbon. Ninety percent of melanoidin removal was achieved through a modified

zeolite adsorbent in the aqueous solution with adsorption capacity ranging from 825 to 1127 mg/g at a rising temperature from 25 to 45 °C (Francisca Kalavathi et al. 2001). Chitin nanofiber shows a maximum adsorption capacity of 131–325 mg/g at varying temperatures (Dolphen and Thiravetyan 2011). Activated carbon prepared by chemical activation of cane bagasse bottom ash succeeded in removing approximately 90% of the melanoidins from an aqueous solution with an adsorption capacity of 200–235 mg/L at increasing temperatures from 5 to 8 °C (Simaratanamongkol and Thiravetyan 2010). Moreover, inorganic-organic hybrid materials have also been investigated for contamination removal (El-Safty et al. 2014). However, these methods had less adsorption capacity and require a greater amount of adsorbent dose.

Fly ash is a major coal-combustion by-product generated in thermal power plants in huge quantities. The global annual fly ash production is about 700 million tons (Krishna Prasad and Srivastava 2009a). Although a significant amount of this portion is being valorized in different applications, such as a substitute for cement in concrete, still, huge quantities are not being utilized and require more proper disposal actions. More productive utilization of fly ash would be beneficial to the environment, as it would decrease water and air pollution. The fly ash discarded in huge amounts in a thermal power plant can be utilized as an excellent adsorbent for the reduction of color-causing compounds (An et al. 2016; Visa et al. 2011).

For the practical application, a packed bed adsorption system is widely used in vapor adsorption, toxic gases, and organic solvents. A most simple packed bed adsorption system comprises a single column filled with a specific type of adsorbent. Recently, a few adsorption simulation softwares are developed for the column simulation at various process parameters; the ASPEN ADSIM V10 is one of them. It is a window-based commercial simulator developed by Aspen tech, used as a simulator for the development of model at various process conditions. The software utilizes a set of algebraic, partial, and ordinary differential equations in order to fully describe the ion-exchange and adsorption column along with appropriate initial and boundary conditions.

In view of the presented literature, this work aims to utilize solid waste from a thermal power station for melanoidin reduction from distillery effluent by adsorption. To accomplish this, coal fly ash was modified through chemical treatment and was then tested for melanoidin adsorption. The present study investigates the adsorption potential of the activated fly ash adsorbent for melanoidin uptake. The mechanism and performance of the melanoidin removal

were evaluated through isotherm and kinetic modeling at various initial concentrations and time, respectively. Additionally, various instrumental techniques were applied to raw and modified coal fly ash such as XRD, BET, and SEM in order to compare the adsorption properties. Moreover, the experimental study results were utilized to develop a comprehensive model of melanoidin adsorption using Aspen Adsim simulation software. The continuous behavior of melanoidin uptake was evaluated through a developed model as a function of different bed height, initial concentration, and flow rate. Hence, it was observed that chemically treated fly ash has a good potential as expected towards melanoidin uptake and could be used to design a commercially packed bed column.

Material and methods

Distillery effluent collection

Real effluent was obtained from a local ethanol-processing industry, situated in the Matiari District, Sindh, Pakistan. The industry employs four full-scale anaerobic digesters for spent wash treatment. Initially, the raw spent wash is put in storage before being placed in anaerobic digesters. The anaerobically treated spent wash is then placed into aeration ponds where water from a different section of the industry is mixed with biodigested spent wash prior to discharge. The wastewater samples for this work were obtained from the discharge line of the bio-digesters before being fed to the aeration ponds. All the samples were stored at 4 °C before being used (Liang et al. 2009).

The detailed schematic diagram of the study is describes in Fig. 1.

Fig. 1

Methodology for experimental analysis

Synthesis of fly ash absorbent

The fly ash samples were obtained from a coal-fired thermal power station. The smallest particle size of fly ash was obtained by applying a sieve set analysis. The sieved fly ash was washed several times using D.I water in order to eliminate pore-clogging and soluble inorganic matter (Bada and Potgieter-Vermaak 2008). Later, washed fly ash was separated from the mixture of fly ash and distilled water by applying a sedimentation process. Further, it was chemically treated 4 times with a 15% diluted sulfuric acid solution and separated from the mixture by filtration using Whatman 42 filter paper. After chemical activation, treated fly ash samples were washed again using deionized water in order to eliminate additional sulfuric acid. Finally, the treated fly ash was placed in an oven for 24 h at 105 °C and then stored in a desiccator.

Characterization

The wide-angle X-ray diffraction (XRD) patterns were examined in a diffractometer using Ni-filtered Cu K α ($\lambda = 0.15418$ nm). The operating voltage of 40 kV and a current of 30 mA were maintained in the diffractometer. The distribution of pore size, pore volume, and surface area was evaluated through N₂ physio-sorption analysis. The N₂ adsorption-desorption and Brunauer-Emmett-Teller (BET) surface area were measured at -196 °C through an automated gas adsorption system. The

Barrett-Joyner-Halenda (BJH) method was used to calculate pore size distributions. All the samples were first degassed at 140 °C for 4 h under the vacuum before the analysis. The scanning electron microscope (SEM) images were recorded for surface morphology of fresh and treated fly ash adsorbent at an acceleration voltage of 10 kV. The results of characterization were used to define properties of the adsorbent in Aspen Adsim simulation software.

Adsorption experimental setup

A number of experiments were performed for kinetic and isotherm modeling to evaluate adsorption behavior and the mechanism of adsorption. In all the experiments, 50 mL of biodigested spent wash was shaken at 120 rpm at a constant temperature of 25 °C in an incubated shaker. The adsorption kinetic experiments were performed at various contact times (30, 60, 90, 120, 150, 180, and 210 min). The concentration of melanoidins in the wastewater was adjusted using D.I water, while the pH of the wastewater was varied by adding 0.1 N of NaOH and H₂SO₄ (Garg et al. 2003). The adsorption study was further performed as a function of pH (2, 4, 6, 8, 10, and 12) and initial concentration (5%, 10%, 15%, 20%, 25%, and 30% dilution). All the batch experiments were replicated three times.

The analysis of melanoidins

The concentration of melanoidins in contaminated water follows the ADMI color index developed by American Dye Manufacturing Institute for the monitoring of the quality of contaminated water. The technique is based on the degree of transmittance in the range of 40 to 700 nm steps in 31 wavelengths (Chandra et al. 2008). Thus, melanoidin concentration in solution was recorded in double beam UV visible spectrophotometer. Prior to analysis, the solution was filtered via Whatman 42 filter paper. The amount of melanoidin uptake by the adsorbent was measured using Eq. 1.

$$q \text{ (mg/g)} = \frac{(C_o - C_e)}{m} \times V \quad 1$$

where C_o represents the concentration of melanoidins before adsorption (mg/L); C_e is the concentration of melanoidins after adsorption process (mg/L); m is the adsorbent mass (mg); and V defines the volume of solution. The percentage of melanoidin removal was quantified using Eq. 2.

$$\% \text{Removal} = \frac{(C_o - C_e)}{C_o} \times 100 \quad 2$$

An error analysis was also performed to compare the validity of isotherms and kinetic models using Eq. 3.

$$\text{SSE} = \sum_{i=1}^n (q_{\text{cal}} - q_{\text{exp}})^2 \quad 3$$

where q_{cal} and q_{exp} are model calculated and experimental adsorption capacities of melanoidins, respectively.

Packed bed column simulation

Aspen ADSIM software was used to develop adsorption breakthrough curves as a function of various melanoidin concentrations, adsorbent bed height, and flow rate; the selected model of adsorption column for simulation is shown in Fig. 2. The initial simulation column flow and feed streams enter into the packed bed column which are assumed to follow the ideal flow pattern; thus, the convective force is responsible for adsorption. The Langmuir isotherm parameters for the adsorbing material which was extracted from the experimental study along with its basic characteristics were used in the simulations; the temperature was assumed constant. The upward difference scheme (BUDS) with 50 nodes was assumed as a different method in order to calculate the model equation. The properties of melanoidins present in feed water were extracted from the literature, described in Table 1.

Fig. 2

The packed bed column model developed in Aspen AdsimV10

Table 1

Properties of melanoidins in distillery effluent (Satyawali and Balakrishnan 2007)

Physical properties	Value
Molecular weight	5000–40,000 Da
Specific gravity	1.2 g/cc
Boiling point	570 °F
Molecular formula	$C_{18}H_{27}O_{10}N$

Assumptions

The following general assumptions were considered for simulation in bed model for liquid adsorption:

- a) Across the column, the behavior of the fluid is assumed as a plug flow, where the molecule flow rate is assumed as constant. Thus, the movement of the subsequent molecules generates a flat velocity profile; therefore, it is considered as an individual CSTR cell.
- b) According to the laminar flow momentum balance, the liquid-phase pressure drop is constant (the pressure drop is assumed as proportional to the velocity of fluid)
- c) The fluid moment throughout the bed is considered as constant; as a result, velocity is also constant.
- d) The molar concentration of melanoidins is calculated from molar volume. The molar volume is considered a linear function of solution composition because of the ideal liquid-phase mixing.
- e) A lumped rate of mass transfer is considered with liquid-phase or solid-film resistance. The resistance could be linear, non-linear, or user-defined. The resistance during adsorption could be linear, non-linear, or user-defined.

Assumption for models

The linear lumped resistance was selected as a model assumption in simulation. It is based on the assumption that the driving force for mass transfer of the components is a linear function of aqueous-phase concentration or solid-phase loading. The mathematical expression is expressed in the following correlation.

Mass balance

The general form of material and mass balance equation for aqueous-phase sorption on adsorbent is written as

$$-\varepsilon_i E_i \frac{\partial^2 c_i}{\partial z^2} + \frac{\partial}{\partial z} (\nu_i c_i) + \varepsilon_i \frac{\partial c_i}{\partial t} + \rho_s \frac{\partial w_i}{\partial t} = 0 \quad 4$$

The first term of the expression indicates dispersion force whereas the second part denotes the convective force responsible in adsorption, and the third term

represents accumulation. The last term of the expression indicated the mass transfer from aqueous phase to solid phase.

$$\frac{\partial w_k}{\partial t} = MTC_{sk} (w_k^* - w_k) \quad 5$$

The convection with constant dispersion

The diffusion of the adsorbate into the adsorbent material can be in different forms; the Aspen Adsim has the list of different dispersion assumptions. In this study, convection with constant dispersion was selected for simulation. In this model, it is assumed that the coefficient of dispersion is constant for each component across the bed.

The isotherm model selection

The performance of the adsorption separation process is depicted in the adsorption equilibrium. Therefore, the adsorption isotherm is one the essential parameters to define the uptake capacity of the adsorbent; thus, it is also an essential designing parameter of the adsorption column. The adsorption equilibrium is a point at which all the vacant sites on the surface of adsorbent is completely filled with solute in solution; as a result, no more adsorption occurs. Therefore, once the isotherm parameters of the specific components are determined, the bed model to define a packed bed column performance at various operating process conditions could be created.

Varying parameters in simulations

The performance of the packed bed column was investigated by performing various dynamic simulations at different operating process conditions. The varying parameters include column height, melanoidin concentration in the feed, and flow rate as described in Table 2.

Table 2

Various simulations cases with their varying parameters

Sr. no.	Concentration (initial)	Inlet flow	Height of bed
	mol/L	Lit/min	m
1	1	50	1.5
2			2

Sr. no.	Concentration (initial)	Inlet flow	Height of bed
	mol/L	Lit/min	m
3		100	2.5
4			1.5
5			2
6			2.5
7		150	1.5
8			2
9			2.5
10	3	50	1.5
11			2
12			2.5
13		100	1.5
14			2
15			2.5
16		150	1.5
17			2
18			2.5
19	5	50	1.5
20			2
21			2.5
22		100	1.5
23			2
24			2.5
25		150	1.5
26			2
27			2.5

Results and discussion

Characterization of raw and treated fly ash adsorbent

The mineralogical arrangement of the fresh and chemically activated fly ash adsorbent was deduced by X-ray diffraction analysis as described in Fig. 3a. The high apex of quartz in the diffractograms of treated and untreated fly ash indicates the high quantity of silicon oxide (SiO_2). Moreover, no significant difference was observed in treated and untreated fly ash adsorbents after chemical activation; the finding was reported by Gieré et al. (2003). In addition, a larger quantity of hematite, mullite, and quartz and a smaller amount of calcium and sodium oxide were found in the untreated fly ash. The high intensity of quartz in fly ash develops a steady and chemically vigorous thick layer on the surface, which protects the inner surface. The inner portion of the fly ash consists of porous particle-sized quantities of carbon, aluminum, and silicon (Sarbak and Kramer-Wachowiak 2002). After chemical activation, this outer layer breaks down, which enhanced the adsorption capacity.

Fig. 3

a The XRD analysis of fly ash adsorbent. **b** Adsorption-desorption of fresh and activated fly ash adsorbent and the BJH pore size distribution. **c** SEM images of raw coal fly ash. **d** Treated coal fly ash adsorbent

The adsorption-desorption isotherms for both fresh and treated fly ash adsorbents are described in Fig. 3b. According to IUPAC classification, all the isotherms can be defined as type IV (Sing et al. n.d.). Besides, their hysteresis loops are of type H3, defining the mesoporous materials. As is clearly observed from the results described in Fig. 3, adsorbed volume increases gradually at a low relative pressure of about 0.06 to 0.6 followed by a sudden increase from 0.6 and above.

AQ3

The pore volume and pore size distribution were quantified through the Barrett-Joyner-Halenda (BJH) model, as shown in Fig. 3b. It can be clearly observed that the pores are mainly located between 2 and 50 nm which confirms the mesoporous structure and also closely related to the sorption isotherm of type IV.

The trend is still not uniform, which confirms that there was a dual mesoporous distribution around 28 and 65 nm. Thus, the pore size of fresh and treated fly ash adsorbent is around 29 and 72 nm, respectively. The results are described in Table 2

Replace Table 2 with Table 3

Both fresh and activated fly ash adsorbents show larger pore volume in the higher pore range (20–70 nm) and smaller pore volume in the lower pore range (2–20 nm). It can be clearly seen that there was a dual mesoporous distribution around 15 and 46 nm. The size distribution shape of both fresh and activated samples revealed related pore texture. However, a narrow pore volume was observed in the case of the fresh sample which confirms the uniform pores. Moreover, the surface area was enhanced from 10.606 to 11.226 m²/g after chemical activation. Furthermore, the results summarized in Table 3 were utilized in defining the properties of adsorbent in Aspen Adsim simulation software.

Table 3

Properties of activated fly ash adsorbent

Characteristics	Value	Unit
Bulk density	0.75	g/cm
Total pore volume	0.1712	cm ³ /g
Microspore volume	0.126	cm ³ /g
Bed porosity	0.428	Dimensionless
Average diameter	73	Nm
BET surface area	11.226	m ² /g
Langmuir equation parameter	K _L (Table 3)	L/mg
	q _m (Table 3)	mg/g

Figure 3 c and d show the scanning electron micrographs for raw and treated fly ash adsorbents at different magnifications. Significantly, it was observed that a large piece of coal fly ash was decomposed into small fragments by the acid activation process (Fig. 3c). The reaction of the acid with metallic oxide and alkali substances (Fe₂O₃, Al₂O₃) might be another potential reason which led to the modification of the whole structure of coal fly ash. Therefore, treated fly ash has a slightly greater surface area than the raw fly ash, which could be confirmed by the BET surface area.

The influence of pH on melanoidin removal

The pH of wastewater is an essential parameter that strongly affects the sorption capacity. The change in pH value affects the surface charge on the adsorbent surface along with ionization degree and speciation of pollutants. Moreover, the functional group on the active sites of adsorbent surface is dissociated by a change in pH, which disturbs the adsorption process. Consequently, this leads to a shift in the equilibrium and kinetics of the overall adsorption process. The influence of melanoidin uptake on to a modified fly ash was evaluated at variable pH values from 2 to 12, as described in Fig. 4. The higher melanoidin uptake was observed at a pH of 6 and gradually decreases at further increases in pH, which illustrates that acid to neutral pH is the best to facilitate overall adsorption.

Fig. 4

The influence of pH on melanoidin uptake (temperature 25 °C, particle size 0.15 mm, shaking time 120 min)

Melanoidin adsorption isotherms

The melanoidin concentration in wastewater is one of the essential parameters that are to be considered in the adsorption process (Chen 2015). Therefore, a sorption study was performed at varying initial concentrations of melanoidins at a known amount of adsorbent dose; the results are illustrated in Fig. 5 a and b. It was observed that at increasing initial concentrations, the removal percent of melanoidins gradually decreased, as shown in Fig. 5a. The reduction in melanoidin removal was due to the limited vacant positions on the adsorbent surface.

Fig. 5

a The influence of initial melanoidin concentration (temperature 25 °C, pH 7, dose 5 g/L, particle size 0.15 mm, adsorbent dose 5 g/L, and shaking time 120 min). **b** Non-linear isotherms

The adsorption isotherm modeling is an important technique to compare and predict adsorption performance and adsorption capacity and to design the overall adsorption process (Chen 2015; Niu et al. 2017). Therefore, the equilibrium performance of the batch experimental data was modeled through two well-known sorption isotherm models: the Langmuir isotherm and the Freundlich isotherm. The equation for Langmuir (Eq. 6) and Freundlich (Eq. 7) can be illustrated as follows:

$$q_e = \frac{q_{\max} K_L C_e}{(1 + K_L C_e)} \quad 6$$

$$q_e = K_F C_e^{1/n}$$

where $q_{\max}$ is the maximum amount of melanoidin uptake by the adsorbent per unit mass of sorbent (mg/g); C_e defines the melanoidin equilibrium concentration in solution (mg/L); K_L represents the Langmuir sorption constant associated with sorption free energy and sorbent-melanoidin affinity (L/mg); K_F signifies sorption capacity per unit concentration ((mg/g)/(mg/L)ⁿ) while, $1/n$ provides information of active sites; the lesser value of $1/n$ specifies the occurrence of heterogeneous sites and that sorption mechanism would be physical in nature (Cao et al. 2014; Gunay et al. 2013; Malhotra et al. 2018). The Langmuir isotherm assumes that the uptake of adsorbate takes place at the finite number of the vacant site present on the surface of the adsorbent. Moreover, one empty site is only filled by one molecule and forms a homogeneous thick layer normally known as monolayer sorption. The Freundlich isotherm model deals with the heterogeneity of the surface of adsorbent towards adsorbent (Gunay et al. 2013; Valix et al. 2009). The adsorption isotherm of melanoidins by treated fly ash adsorbent was plotted and as shown in Fig. 5 a and b, the batch experimental data fit the widely used Langmuir and Freundlich isotherm models.

The related isotherm parameters were deduced by performing a non-linear regression analysis; the calculated values are summarized in Table 4. It was found that the melanoidin uptake was best described by the Langmuir isotherm model, which was also confirmed by the greater R^2 value. Besides this, the experimental adsorption capacity ($q_{\text{exp}} = 289.42$) was very close to the model calculated adsorption capacity ($q_{\max} = 281.34$). Therefore, it can be deduced from the results that there is a development of a monomolecular layer of melanoidins on the adsorbent surface, during adsorption. In addition, it was also observed that chemisorption occurred, which confirms that the chemisorption is responsible for melanoidin uptake (Goscianska et al. 2016).

Table 4

Isotherms parameters

Exp	Langmuir					Freundlich				
q_{exp} (mg/g)	q_m (mg/g)	K_L (L/mg)	R^2	Std	SSE	n	K_f (mg/L)	R^2	Std	SSE
289.42	281.34	0.00233	0.95	0.25	0.36	2.56	12.47	0.90	0.15	0.61

Adsorption kinetics

A kinetic experimental study was performed in order to determine the effect of contact time and the sorption mechanism of melanoidins on a treated coal fly ash adsorbent. A fast adsorption rate was found in the initial 30 min of contact time, owing to a large number of empty sites available initially on the adsorbent surface. Later, a significant decrease in the rate of adsorption was observed and the adsorption process reached to equilibrium point at 120 min of contact time. After reaching equilibrium, the remaining empty sites on the adsorbent surface are too complex to be filled, because of the repulsive force between melanoidins on the surface and in solution. Therefore, further adsorption of melanoidins ceases (Erto et al. 2015; Yu et al. 2003).

To better comprehend the kinetic behavior of melanoidin reduction by adsorption, experimental kinetic data was modeled through the pseudo-first-order and pseudo-second-order kinetic models, as illustrated in Fig. 6 b and c, respectively. The non-linear form of both models is described in Eqs. 8 and 9, respectively (Chowdhury and Das 2011).

$$q_t = q_e (1 - \exp^{-k_1 t}) \quad 8$$

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad 9$$

where q_t defines the melanoidin uptake at time t (mg/g); t represents constant time (min); k_1 is the rate constant of the first-order kinetic model (min^{-1}); and K_2 defines the rate constant of the second-order kinetic model ($\text{gm}/(\text{mg min})$). The first-order kinetic model is generally based on the assumption that the organic pollutant adsorption on the surface of the adsorbent can be considered as reversible with equilibrium being achieved (physio-sorption). Additionally, the second-order kinetic model assumes that a chemical bond is developed during adsorption due to the sharing of electrons between solute and adsorbent (chemisorption) (Maneerung et al. 2016; Zhao et al. 2017).

Fig. 6

a The effect of contact time (pH 7, temperature 303 K, shaking time 30–240 min, dosage 5 g per 50 mL). **b** First-order kinetics. **c** Second-order kinetics. **d** Inter-particle diffusion models

Generally, the solid-liquid adsorption mechanism is comprised of three steps; one or any of them could be a rate-limiting step. The three steps are the following: (i) mass transfer, (ii) the binding force of the solute and adsorbent defines the energy required in adsorption and overall behavior of adsorption process (physical/chemical); and (iii) melanoidin diffusion to the surface of adsorbent may be either by a pore diffusion or by the solid surface diffusion [38–39]. Therefore, kinetic behavior was further evaluated using the IDP model to better define the adsorption mechanism. The linearized graph between q_t and $t^{1/2}$ is shown in Fig. 6d and the model equation (Eq. 10) is described below.

$$q_t = K_i t^{1/2} + C$$

where K_i denotes the rate constant and C denotes the line intercept. The C value gives information about the boundary layer thickness. The maximum effect on the boundary layer will be observed at a higher value of C (Kavitha and Namasivayam 2007). The IDP rate constant revealed that the diffusion mechanism of the melanoidin uptake by treated fly ash adsorbent is significantly affected by the boundary layer.

The related parameters of the models were calculated through the regression analysis; the results are described in Table 5. It was observed that the kinetic behavior of the melanoidin uptake was best described by the second-order kinetic model which confirms the co-occurrence of physical as well as chemical interaction (Koby 2004). Furthermore, the IDP plot ($t^{0.5}$ vs. q_t) shown in Fig. 6d is not linear throughout the range of kinetic time. Moreover, the two phases in the plot of intra-particle diffusion model revealed that melanoidin sorption on to treated fly ash adsorbent proceeds with surface sorption and intra-particle diffusion. The initial part of the curve describes the boundary layer effect and the sound portion of the curve demonstrates the intra-particle diffusion of the melanoidins into the pores of adsorbent.

Table 5

Kinetic parameters

First-order kinetic					Second-order kinetic					Intr
q_e (mg/g)	k_1 (min ⁻¹)	R^2	Std	SSE	q_e (mg/g)	k_2 (mg/g/min)	R^2	Std	SSE	k (mg/g/l
78.36	0.0528	0.95	1.24	1.29	84.034	0.0141	0.98	0.34	0.24	4.52

Comparative adsorption study

The related studies for melanoidin adsorption were compiled to compare the sorption capacity and sorption saturation time, as given in Table 6. It was appraised from compiled results that acid-treated coal fly ash adsorbent showed higher sorption capacity (281.9 mg/g) towards melanoidins as compared with other adsorbents used in previous studies. Furthermore, adsorbent saturation time is also one of the essential parameters in describing the practical application of an

adsorbent. Thus, the results of this study revealed that adsorbent has the lowest sorption saturation time as compared with compiled studies.

Table 6

Comparison of results with literature

Materials	Adsorption capacity $q_{\max}$ (mg/g)	Saturation time (min)	Reference
Treated coal fly ash	281.9	120	This study
Chitin nanofiber	131.2	120	(Dolphen and Thiravetyan 2011)
Activated bagasse bottom ash	208.2	240	(Simaratanamongkol and Thiravetyan 2010)
Commercial activated carbon	232.08	(8 days) 11,520	(Figaro et al. 2009)
Fly ash-clay	170.2	420	(Ramezani et al. 2011)

Influence of bed heights on breakthrough curve

The effect of column bed height (1.5, 2, and 2.5 m) on melanoidin adsorption at a varying feed flow rate (50, 100, and 150 lit/min) with a constant initial concentration of melanoidins (1 k mol/lit) is shown in Fig. 7a–c. Similarly, Figs. 8a–c and 9a–c show the effect of bed height at constant melanoidin concentration of 3 mol/lit and 5 mol/lit, respectively. At the increasing bed height of the column, the saturation time of adsorbent and breakthrough time are enhanced because of the higher number of vacant sites availability. Thus, at larger bed height, the molecules of solute have a higher residence which facilitates the penetration of solute within the pores on the adsorbent surface. The higher uptake of melanoidins was found at a bed height of 2.5 m and a flow rate of 50 lit/min.

Fig. 7

a–c The effect of bed height at different inlet flow conditions (pH 7, temperature 25 °C, particle size 0.15 mm) at melanoidin concentration of 1 mol/lit

Fig. 8

a–c The effect of bed height at different inlet flow conditions (pH 7, temperature 25 °C, particle size 0.15 mm) at melanoidin concentration of 3 mol/lit

Fig. 9

a–c The effect of bed height at different inlet flow conditions (pH 7, temperature 25 °C, particle size 0.15 mm) at melanoidin concentration of 5 mol/lit

Influence of the feed flow rate on breakthrough curve

Figures 10, 11, and 12 a–c show the effect of feed flow rate on melanoidin uptake at varying column height in the range of 1.5 to 2.5 m with a constant initial melanoidin concentration of 1 to 5 mol/lit. At the increasing feed flow rate, the breakthrough curve becomes steeper which results in a decrease in breakthrough time and adsorption saturation time. The continuous adsorption behavior in a column can be described as the melanoidin uptake within the pore of adsorbent is influenced due to the insufficient contact time, molecule diffusion inside the pores, and limited active sites on the surface of adsorbent (Jahangiri-Rad et al. 2014). Therefore, at the higher flow rate, melanoidin solution leaves the column before reaching the equilibrium. In general, highest melanoidin uptake was found at decreasing feed flow rate. The maximum melanoidin uptake was found at 50 lit/min feed flow rate and a bed height of 2.5 m.

Fig. 10

a–c The effect of inlet flow conditions at different bed heights (pH 7, temperature 25 °C, particle size 0.15 mm) at melanoidin concentration of 1 mol/lit

Fig. 11

a–c The effect of inlet flow conditions at different bed heights (pH 7, temperature 25 °C, particle size 0.15 mm) at inlet melanoidin concentration of 3 mol/lit

Fig. 12

a–c The effect of inlet flow conditions at different bed heights (pH 7, temperature 25 °C, particle size 0.15 mm) at inlet concentration of 5 mol/lit

Influence of inlet melanoidin concentration

The effect of varying initial melanoidin concentration on adsorption at different flow rates with constant bed heights of 1.5, 2, and 2.5 m is shown in Figs. 13, 14, and 15, respectively. In this case, breakthrough curves are plotted between effluent concentration and time because the ratio of effluent to influent melanoidin concentration (C_e/C_o) becomes similar in all cases (Anisuzzaman et al. 2016). A decline in adsorption saturation and breakthrough time were observed at varying melanoidin concentration and feed flow rate to the column. It was observed that at increasing melanoidin concentration and flow rate, breakthrough time and adsorption saturation time were decreased. The maximum breakthrough time and adsorption saturation time were observed at initial melanoidin concentration of 3 mol/lit and flow rate of 50 lit/min. Whereas, lowest adsorption saturation time and breakthrough time were observed at an initial concentration of 5 mol/lit and flow rate of 150 lit/min.

Fig. 13

The effect of melanoidin concentration and flow rate (pH 7, temperature 25 °C, particle size 0.15 mm) at bed height of 1.5 m

Fig. 14

The effect of melanoidin concentration and flow rate (pH 7, temperature 25 °C, particle size 0.15 mm) at bed height of 2 m

Fig. 15

The effect of melanoidin concentration and flow rate (pH 7, temperature 25 °C, particle size 0.15 mm) at bed height of 2.5 m

Conclusions

The reduction of melanoidins by the chemically activated fly ash adsorbent in actual distillery effluent was observed and measured. The adsorption performance was optimized at various melanoidin concentrations, initial effluent pH, and contact time. Packed bed column performance was optimized as a function of different bed height, flow rate, and feed concentration. The experimental results revealed that coal fly ash is a good adsorbent for melanoidin degradation (84%) from distillery wastewater. The adsorption mechanism best follows the Langmuir isotherm model with a higher R^2 value of 0.99, which confirms the monolayer adsorption through electrostatic interaction and worked best with an acidic to neutral pH. The best removal percent was found at pH 6. The contact time needed for adsorption equilibrium was 120 min. The adsorption kinetic best follows the pseudo-second-order kinetic models, which indicates that the adsorption mechanism follows both physical and chemical adsorptions. The maximum breakthrough time and adsorbent

saturation time were achieved at initial melanoidin concentration of 1 mol/lit, column height of 2.5 m, and a flow rate of 50 lit/min.

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