COD and colour removal from molasses spent wash using activated carbon produced from bagasse fly ash of Matahara sugar factory, Oromiya region, Ethiopia

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ABSTRACT

The aim of this study was to investigate the removal of chemical oxygen demand (COD) and colour from a melanoidin solution using activated carbon produced from bagasse fly ash (BFA). Melanoidins are heterogeneous polymers and major contributors to the dark brown colour of molasses spent wash, which is an extensive cause of environment pollution. The surface area of the BFA was determined as 160.9 ± 2.8m²/g with 90% of particle less than 156.8 µm in size. Characterization of the BFA by Fourier transform infrared spectroscopy (FTIR) showed the presence of hydroxyl and carbonyl functional groups, whereas X-ray diffraction analysis indicated its amorphous nature. Moreover, scanning electron microscopy analysis showed a heterogeneous and irregular shape of pores. Among the adsorption isotherm models analysed, the Freundlich model fitted best to the experimental data, indicating a maximum adsorptive capacity of 124.80 mg/g. The removal of COD and colour from a melanoidin solution with this activated carbon was carried out using an experimental design taking 4 factors into account. These were adsorbent dose, contact time, pH and initial COD concentration, with removal of COD and colour as response variables. COD reduction was influenced by initial COD concentration whereas colour removal was dominated by contact time, which was in line with the findings of principal component analysis . The maximum COD removal recorded was 61.6% at the optimum condition of adsorbent dose of 4 g in 100 mL, contact time of 4 h, pH 8 and initial COD concentration 6 000 mg/L, whereas the decolourization of melanoidin solution was 64% at adsorbent dose of 4 g, contact time 4 h, pH 3 and initial COD concentration 6 000 mg/L. Hence, activated BFA is a promising option for simultaneous removal of COD and colour from molasses spent wash under the stated conditions.

Keywords: adsorption; factorial design; distillery spent wash; melanoidins; optimization; COD and colour removal

INTRODUCTION

Fossil fuel depletion and concerns over climate change and energy security have stimulated interest in more sustainable and low-carbon energy production in various countries around the world (Chooyok et al., 2013). Bioenergy is the carbon-neutral and renewable energy resource that can be converted into any form of fuel for utilization. Globally, ethanol distillery industries are growing rapidly to satisfy the increasing demand for sustainable and renewable biofuel, particularly bioethanol (David et al., 2015). The estimated global demand for bioethanol in 2020 will rise beyond 1.2 × 10^{11} L and molasses make up the largest portion of the feedstock for distillery industries, as indicated by Arimi et al. (2015). However, ethanol distillery industries generate large volumes of high-strength wastewater, termed molasses spent wash. The ever-increasing generation of molasses spent wash results in unwanted residual liquid waste that poses a serious threat to the water quality and soil properties in several regions around the globe (Mohana et al., 2009). The imposition of stringent environmental regulations and environmental demand for bioethanol are driving forces in the treatment of molasses spent wash using different technologies (Kazemi et al., 2015).

For every litre of ethanol production, about 15 L of molasses spent wash is generated (Yadav et al., 2011). Spent wash is very acidic in nature, highly charged in organic matter, and is considered to be a troublesome and complex industrial wastewater (Mohana et al., 2007). Generally, distillery spent wash is classified as high-strength industrial wastewater and environmentally considered as 'red' category waste, due to its high content of organic matter with very low degradability. For instance, a COD range of 110 000–190 000 mg/L) and BOD range of 50 000–60 000 mg/L for molasses spent wash has been reported (Acharya et al., 2008). Another peculiar feature of the spent wash is its colour, which is deep dark brown. The colour of spent wash is mainly due to melanoidins, which account for 2% of total spent wash by mass (Naik et al., 2010). Colour removal is a challenge for melanoidins containing distillery wastewater.

Melanoidin is the final product of the dehydration and condensation of sugar and amino acids under non-enzymatic

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(Maillard chemical) reactions (Wang et al., 2011). It is a recalcitrant, antioxidant, acidic, nitrogen-containing dark brown polymeric compound (David et al., 2015). The molecular weight of melanoidin is estimated to be between of 5 000 and 40 000 Da, having an empirical formula of $C_{17–18}H_{26–27}O_{10}N$ (Krishna Prasad and Srivastava, 2009). Molasses-based ethanol distillery spent wash is the major source of melanoidin wastewater (Yadav et al., 2011).

Discharge of untreated melanoidin-containing spent wash can block sunlight in water bodies, which results in reduced photosynthetic activity and oxygen concentration, which inhibits the survival of aquatic life (Dahiya et al., 2001). Hence, distillery spent wash which contains melanoidins has to be treated prior to discharge into the natural environment to prevent water pollution and ecological impacts, although removal with different treatment methods is challenging. Spent wash colour removal by conventional wastewater treatment is an unsolved issue (Arimi et al., 2014). Moreover, melanoidins have antioxidant and antimicrobial properties that suppress the growth of bacteria, which in turn can result in very low biodegradation (Rufián-Henares and Morales, 2007). Among many treatment methods, ozone treatment technology for distillery spent wash is effective. However, wastewater treatment by ozonation is not always feasible because of the high operational cost and demand for electricity. Adsorption is another physicochemical treatment technology which is frequently used in water and wastewater treatment. It is a powerful and efficient technique in the removal of organic matter and colour from industrial wastewaters (Kushwaha et al., 2010) but the great limitation is the cost. Hence, many studies are looking into the production of low-cost, efficient adsorbents derived from easily available materials such as industrial solid wastes and by-products.

Bagasse fly ash (BFA) is industrial solid waste generated from burning of bagasse in steam boilers to generate electric energy in the sugar industry. In most developing countries, BFA is not commercialized and remains as a waste that causes great problems for environmental disposal. Studies have shown that it is a carbon- and silica-rich industrial waste which is cheap and available in large quantities in many sugar industries (Mall et al., 2005). It has been used as an adsorbent for removal of heavy metals, organic matter and dyes from water and wastewater under different treatment conditions. For instance, for adsorption of acrylonitrile from aqueous solution (100 mg/L) BFA has been used as an adsorbent with surface area of 379.64 m^2/g and giving 78% removal efficiency (Kumar et al., 2014). A treatment efficiency of 99.16% was also achieved for removal of copper ion from aqueous solution at 77.88 mg/L initial copper concentration (Ghosh and Saha, 2015).

Application of BFA for pulp and paper industry effluent treatment was studied and adsorptive removal efficiencies of 50% and 55% for COD and colour, respectively, were reported (Srivastava et al., 2005). In another study, BFA proximate moisture content was recorded as 7.64%, volatile matter 17.37%, ash 26.43%, fixed carbon 48.56% and bulk density 133.3 kg/m^3 (Srivastava et al., 2006). The low value of fixed carbon (19.20%) and high ash content (72.60%) were also reported (Chandra et al., 2007). With respect to BFA adsorbent development, a surface area of 168.83 m^2/g was developed and its effectiveness tested for removal of malachite green dyes from aqueous solution. Results revealed an adsorption capacity of 9.971 mg/g (Mall et al., 2005). But adsorption capacity of the BFA is variable due to burning of bagasse in different steam boilers; the variety and composition of the sugarcane used also generates different characteristics for BFA (Srivastava et al., 2005). Generally, activated carbon preparation from BFA has been studied intensively using physical (steam and CO_2) and chemical (KOH, H_2O_2, HCl, EDTA and HNO_3, etc.) processes, but the practical utilization of this resource as an effective treatment option in sugar and ethanol industries for recycling of waste is limited (Purnomo et al., 2012). Moreover, the efficiency of the adsorption technology of activated carbon depends on the nature of the adsorbent, activating agent and activation condition, which generate different surface areas and pore volumes for the interactions between the adsorbate and adsorbent (Gottipati and Mishra, 2010).

Adsorption performance without adsorbent surface modification is low. For instance, untreated BFA vs. that chemically modified with HCl and HNO_3 resulted in adsorption capacities of 19.8, 47.6 and 25.1 mg/g, respectively, when used for removal of Cd (II) from aqueous solution (El-Sherif and Fathy, 2013). Treating biosorbents such as BFA with hydrogen peroxide is known to increase the adsorption capacity nearly threefold(Nagda and Ghole, 2009). Furthermore, hydrogen peroxide can increase the positive valence by electron removal (Chapman, 2003), which is expected to enhance the treatment of negatively-charged (acidic) melanoidin solutions. Hence, activating carbonaceous material using hydrogen peroxide is effective in removing unwanted organic matter on the surface of BFA and the residue of hydrogen peroxide on the adsorbent surface has no significant environmental impact.

Most of the studies conducted so far on distillery spent wash have focused on either colour removal or COD reduction, although both aspects should be studied together for cost effectiveness. Therefore, the main aim of this study was to investigate the optimum conditions for both COD and colour removal from melanoidin solution by batch adsorption on activated BFA. Hence, the experimental design considered 4 factors: pH, adsorbent dose, initial COD concentration and contact time. These factors were studied using a full factorial experimental design. The main advantages of using this approach are the low cost, minimum number of experiments, reduced treatment time and possibility to investigate interaction effects.The physicochemical characterization and the properties of the adsorbent produced are also investigated and reported.

METHODS

Adsorbent development

Bagasse fly ash was collected from the dumping site of the Metahara sugar factory in the regional state of Oromiya (Ethiopia). It was taken to the laboratory and sun-dried for 2 days. Part of the dried BFA was soaked in hydrogen peroxide (30% by concentration) at 60°C for 24 h to remove the organic matter for surface modification. Then it was repeatedly washed with de-ionized water until all hydrogen peroxide on the surface was removed. This modified BFA was placed into an oven at 100°C until it was dried completely. Finally, it was powdered, sieved and stored in a vacuum desiccator until use (Gupta et al., 2002).

Adsorbent characterization

Proximate analysis

Proximate analysis of BFAwas as per standard method of ASTM (Milne et al., 1990). The ash content, moisture and volatile matter of the adsorbent were calculated directly, whereas the amount of fixed carbon was calculated as the difference between the initail total mass adsorbent and the sum of the mass of volatile ash and fixed carbon (Nwabanne and Igbokwe, 2012).

Particle size determination

Particle size distribution was measured based on the principle of laser diffraction, which is capable of measuring particle sizes between 20 nm and 2000 µm according to Malvern Master Sizer Manual (Mastersizer 2000 User Manual 2007).

Fourier transform infrared spectroscopy (FTIR)

A small amount of the adsorbent sample was mixed with dry KBr in the ratio of 2:200 and ground. The well-mixed sample was placed on a ZnSe crystal and pressure was applied. Then the sample was scanned over a wavelength of 600 – 4 000 cm^{-1} by an attenuated total reflection FT-IR (ThermoNicolet 5700). The spectrum of FTIR was obtained at the scanning rate of 32 times/min with a 4 cm^{-1} resolution (Dolphen and Thiravetyan, 2011).

Elemental analysis

For CHNS elemental analyses, 2 mg of the adsorbent sample was mixed with 5 mg of catalyst (VO_5) and placed into a tin cup, whereas for oxygen analysis, 2 mg of sample was placed into a silver cup without VO_5. Then the sample was burned in a column at different temperatures according to the standard methods of the instrument (Thermo Scientific FLASH 2000 CHNS/O elemental analyser). The degassed samples were separated and the chromatograms were created. Finally, the mass percentage of each element was calculated (Tezcan et al., 2015).

Determination of specific surface area

A sample of 0.1 g of BFA was mounted on the port of a TriStar II (TriStar II Series, Micromeritics Instrument Corporation) and degassed overnight at 120°C under vacuum. Then it was placed into liquid nitrogen at −196.15°C and the increased uptake of N_2 was measured. The surface area of the adsorbent was calculated using the BET method in the range of (p/p_0) of 0.05–0.20 (Tezcan et al., 2015).

Scanning electron microscope (SEM) analysis

A surface morphology of adsorbent (BFA) was determined using SEM and SEI resolution 1.0 nm guaranteed at 15 kV (JEOL JSM-7600F FEG-SEM, JEOL, USA). The sample was applied on carbon tape, and measured at a working distance of 8 mm.The sample preparation and analysis were done as per standard operating procedures of JEOL JSM 7600F SEM which was operated at 15 kV and a current of 10 A under 1 000 X magnifications (Hegazy et al., 2014).

X-ray diffraction (XRD) analysis

X-ray powder diffraction (XRD) was used for phase identification of the crystalline nature of BFA. XRD analysis of the BFA sample was conducted using an ARL X'TRA powder diffractometer instrument (Thermo Scientific ARL X'TRA Powder Diffractometer, Massachusetts, USA). The x-ray diffractograms were taken using Cukα radiation at a scanning rate of 1°/min in the range 5−60° 2θ at continuous mode of measuring. The XRD diffractometer was switched on at initialization power 15 kV and 5 mA; and the wavelength of the analysis was fixed at 1.541 nm.

Preparation of melanoidin solution

Synthetic melanoidins were prepared by mixing 4.5 g of glucose (G8270 D-(+), Sigma-Aldrich), 1.88 g of glycine (G7126, Sigma-Aldrich) and 0.42 g of sodium bicarbonate in 100 mL of distilled water which was heated for 7 h at 94.85°C until dried. Then 100 mL of distilled water was added to form a melanoidin solution (Bernardo et al., 1997). Diluted solutions of melanoidin were then prepared according to the initial concentrations required for the optimization process and the pH was adjusted using 0.1 M NaOH and 0.1 M HCl solutions.

Adsorption equilibrium isotherms

Equilibrium isotherm experiments were undertaken in a batch adsorption system under optimum conditions of initial COD concentration 6 000 mg/L, pH 8 and contact time 4 h, but the adsorbent dose was changed from 0.5 to 5 g in 100 mL. Observed values were compared to different adsorption isotherms. The fundamental principle of adsorption isotherms is a set of assumptions that are related to the heterogeneity or homogeneity of the solid surface and the possibility of interaction between the adsorbate species and adsorbents. In this work, Freundlich and Langmuir's isothermal models were used, which are the most commonly applied models in water and wastewater treatment. The amount of adsorbate attached on the surface of the adsorbent is expressed as follows:

$$q_e = \left(\frac{C_0 - C_e}{m}\right)V \tag{1}$$

where: q_e is adsorbate uptake at equilibrium (mg/g), C_0 and C_e are the initial and equilibrium concentrations (mg/L), respectively; V is the volume of adsorbate solution (L) and m is the sorbent mass (g) (Kumar et al. 2014).

The Langmuir equation was developed from the adsorbate equilibrium between the liquid and adsorbent surface (Lata et al., 2008). The general equation is as follows:

$$q_e = \frac{Q_0 C_e K_l}{1 + C_e K_l} \tag{2}$$

The linear form of the equation is:

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{Q_0 C_e K_l} \tag{3}$$

where: C_e is the equilibrium concentration (mg/L), Q_0 maximum the adsorption capacity (mg/g), q_e absorptivity capacity (mg/g), and K_l the Langmuir isotherm constant (L/mg). In this equation, the graph of $\frac{1}{q_e}$ vs $\frac{1}{C_e}$ was plotted; Q_0 and K_l were constants, which can be calculated from the intercept and slope of the equation, respectively.

The Freundlich isothermal model is based on the principle of heterogeneous surface of adsorbents (Simaratanamongkol and Thiravetyan 2010). The equation is as follows:

$$q_e = k_f C_e^{1/m} \tag{4}$$

The linear form of the equation is:

$$\log qe = \log k + \frac{1}{n} \log ce \tag{5}$$

where: q_e (mg/g) is the adsorbed amount of the adsorbate per unit mass of the adsorbent, C_e (mg/L) is the equilibrium concentration in mg/L, K_f ((mg/g) (L/mg)$^{1/n}$) is the Freundlich constant which is associated with the adsorbent capacity of the adsorption and n (unitless) is the Freundlich constant which is directly related to favourability of the adsorption process.

Optimization of batch adsorption

Batch tests were carried out by adding 100 mL of adsorbate (melanoidin) solution to 250 mL conical flasks using 16 different combinations of the upper and lower values of the factors. Flasks were agitated at 160 r/min using an orbital shaker. The solution was then centrifuged at 3 500 r/min for 30 min. Finally, the solution was filtered using Whatman filter paper 42 (pore size 2.5 µm). The filtrate was collected for further COD and colour analysis as per standard methods (APHA, 1998). In the first set of experiments, a screening of the most important factors, i.e., initial COD concentration, adsorbent dose, contact time and pH, was performed. The design of this experiment was a 2^4 full factorial design with 16 runs (Table 1), which was conducted at room temperature. Colour removal and COD reduction of melanoidin solutions were chosen as response variables. The experiments were performed in a random manner with the lower and higher values corresponding to (−1) and (+1), respectively. The levels of each factor were selected based on the literature values (Maurice, 2012).

TABLE 1
Selected factors for full factorial design

Factors	Code	Low(−)	High(+)
Concentration (mg/L)	X_1	1 000	6 000
Adsorbent dose (g in 100 mL)	X_2	1	4
pH	X_3	3	8
Contact time (h)	X_4	1	4

COD and colour analysis

For colour analysis, the absorbance of the filtrate sample was determined at the characteristic wavelength of 475 nm using a double beam UV–Vis spectrophotometer (Agilent technology, Cary 100 UV-Visible Spectrophotometer) (Krishna Prasad and Srivastava, 2009). The colour removal percentage was calculated based on the value of initial melanoidin solution and its value after the adsorption treatment, whereas the COD reduction measurement was made using the initial COD concentration and its value after passing through the treatment by open reflex method (APHA, 1998).

Statistical analysis

The experimental results were analysed by linear regression. Colour removal and COD reduction were considered as response variables (Y) and the removal efficiency of response variables was given by the following equation

$$\begin{aligned} &Y_{\mathrm{COD/Colour}} \\ &= b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4 + b_5X_1X_2 + b_6X_1X_3 \\ &+ b_7X_1X_4 + b_8X_2X_3 + b_9X_2X_4 + b_{10}X_3X_4 + b_{11}X_1X_2X_3 \\ &+ b_{12}X_1X_2X_3 + b_{13}X_1X_3X_4 + b_{14}X_2X_3X_4 + b_{15}X_1X_2X_3X_4 \end{aligned}$$

where: Y_{COD} and Y_{colour} are the response variables for COD and colour, respectively, b_o is the mean of the measurements and b_i is the regression coefficient of the main and interaction effects. The significance of the regression model was checked using analysis of variance (ANOVA) at 95% confidence level. The coefficient of determination, R^2, and adjusted coefficient of determination were used to determine the fit between the model and experimental data. Generally, the model equation was used to identify the influence of the experimental factors and their interaction on colour and COD removal. For statistical analysis with principal component analysis (PCA), the software program SPSS version 23 was used (www.ibm.com). PCA was used to select the most discriminating parameters and to investigate the overall variation of the data (Van Hulle and Ciocci, 2015). PCA was also used as a pattern recognition method aimed at reducing a large number of variables to a smaller number of representative variables (principal components) (Brereton, 2003). Varimax normalised rotation of principal components was carried out in order to reduce the contribution of variables with minor significance and increase the interpretability of the components. In total, 6 factors (COD removal, colour removal, initial COD concentration, adsorbent dose, contact time and pH) were considered. Sixteen batch adsorption experiments were used for this PCA. This ensured that the ratio of the number of experiments to number of factors was relatively low (2.66) compared to a common ratio of 5/1. The Kaiser–Meyer–Olkim criterion for sampling adequacy (KMO) and the Bartlett test were used to verify that correlations between items were sufficiently large for PCA (Hair et al. 1998). The KMO value was 0.4 (< 0.5), indicating that the correlations between the variables were relatively low for application of PCA. On the other hand, the Barlett's test of sphericity (p = 0.05) indicated that the correlations between factors were sufficiently high for PCA.

RESULTS AND DISCUSSION

Elemental and proximate analyses

Elemental analyses of BFA were carried out before and after the treatment with melanoidin-containing wastewater (Table 2). The carbon content of BFA was high (60% by mass) for locally prepared activated carbon but smaller than commercial activated carbon. However, the compositions of hydrogen, nitrogen and sulphur were low and comparable with the values of commercially activated carbon (Alothman et al., 2011). This indicated that BFA is a carbon-rich substance and

TABLE 2
Elemental analyses of BFA before and after treatment

Element	BFA before treatment %	BFA after treatment %
Carbon	60.04	59.03
Hydrogen	0.62	0.71
Nitrogen	0.28	0.34
Oxygen	6.77	14.54
Sulphur	0.00	0.00
Others*	32.29	25.38

**The result was calculated by difference (percentage by mass)*

good precursor for activated carbon. There was an observable change in oxygen percentages before and after the treatment. The raised oxygen might be attributed to the contribution of pollutants from wastewater. Moreover, the study results also showed that 32.29% of BFA composition by mass was made up of other elements.

Proximate analysis is used to identify the amount of fixed carbon and non-carbon sources in the adsorbent. The ash content indicates the amount of inorganic substance that remains after the sample was burned off at high temperature whereas the amount of fixed carbon is the non-volatile carbon source of the adsorbent. The proximate analysis of BFA was given as a percentage by weight (Table 3). These include moisture content (7.64%), ash (26.43%) and volatile substances (17.23%), which are in good agreement with the literature (Mall et al., 2005). However, the amount of fixed carbon (42.2%) was higher than many adsorbents but still smaller than the commercial activated carbon (Hesas et al., 2013). This result indicates that BFA is a good precursor for adsorbent development and helpful in water and wastewater purification.

TABLE 3
Proximate analyses of BFA before and after treatment

Proximate analysis	Mass in %
Moisture	5.0
Volatile matter	16.8
Ash content	36.0
Fixed carbon*	42.2

**The result was calculated by difference (percentage by mass)*

Surface area and particle size determination

Surface area of BFA was measured by adsorption-desorption of nitrogen gas at constant temperature. The amount of nitrogen gas adsorbed is proportional to the surface area of the adsorbent. BFA surface area analysis was carried out before and after the treatment with the melanoidin solution. The observed data were found to be a good fit with the BET model ($R^2 = 0.99$). The experimental results for surface area were 160.9 ± 2.8 m^2/g and 72.8 ±1.0 m^2/g before and after treatment with melanoidin solution. This showed that, of the total surface area, only 55% was occupied by the adsorbates as the result of treatment with the melanoidin solution. This observed value of BET surface area of BFA was average and comparable with literature values of 168.83 m^2/g and 51 m^2/g reported by Mall et al. (2005) and Deokar et al. (2016), respectively. Adsorbent particle size is another important factor that plays a significant role in the adsorption process. According to the standard derived diameter of spherical particles, 10% of the adsorbent sample was smaller than 9.5 μm in diameter and 50% of the sample was less than 36.7 μm. The majority (90%) of adsorbent particle sizes were less than 156.8 μm; average particle size was 61.1 μm. These fine adsorbent particles developed more surface area, enabling fast diffusion of adsorbate to activated sites resulting in faster adsorption kinetics (Madu and Lajide, 2013)

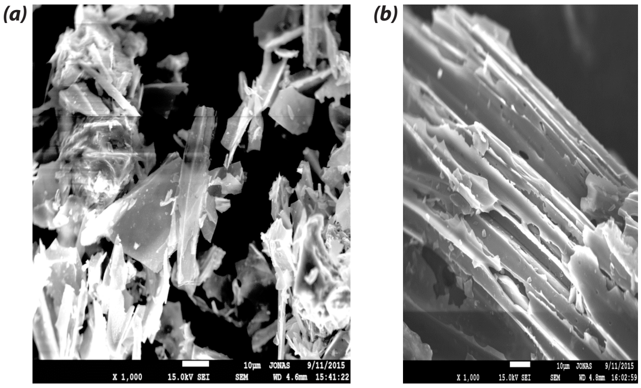

Figure 1
SEM images of BFA before adsorption treatment ***(a)*** *and after treatment* ***(b)*** *(x 1 000)*

SEM analyses

SEM analysis of BFA was performed before and after treatment with melanoidin wastewater (Fig. 1). Shape and the pore size on the surface of BFA were not uniform but heterogeneous and irregular in shape. In particular, the larger-sized pores were rough with a lot of cracks which indicated binding sites for adsorbates of different sizes. This was a good indicator of the development of surface porosity and the readiness of the adsorbent to interact with adsorbates, but the chemical nature of the BFA surface is another important factor to be considered. The BFA surface was magnified 1 000 times, indicating different pores with the potential to accumulate adsorbate of various sizes and shapes. Moreover, surface porosity was clearly diminished after treatment with melanoidin solution, which in turn proved the attachment of pollutants on the surface of the adsorbent.

Fourier transform infrared spectrophotometry (FTIR) analysis

FTIR analysis of the BFA sample revealed only two clearly observable peaks. The first broad and long peak was obtained at 3 255 cm^{-1}, in the range of 3 570–3 200 cm^{-1}. This broad peak represents a hydroxyl group in which the hydrogen bond exists in the stretched form. Additionally, an FTIR library search indicated the primary aliphatic alcohol group. The alcohol functional group can be found at 3 650–3 200 cm^{-1} which was a long and broad peak. This might be attributed to surface oxidation of BFA by hydrogen peroxide. The other peak was found at around 1 700 cm^{-1}, which was associated with C=O bond in the range of 1 650–1 800 cm^{-1}. This group consists of unsaturated aldehydes, ketones, esters and carboxyl functional groups. It gives the hint that hydrogen peroxide led to the surface oxidation and produced the oxygen-bearing functional groups. The chemical activation process for the adsorbent can also break the bond of many functional groups and eliminate volatile and light substrates from the adsorbent surface.

X-ray diffraction (XRD) analysis

X-ray diffraction analysis of BFA was conducted at 2θ in the range 5–60°, which indicated the amorphous nature of the BFA sample with low content of inorganic constituents. There was no significant change in the spectral pattern of the XRD of BFA before and after treatment with melanoidin solution but insignificant peaks were observed which were not clearly identified.

Adsorption isotherms

Analysis of experimental data using different isothermal models provides fundamental knowledge of the adsorption process and adsorption capacities. The equilibrium data were analysed with the Langmuir and Freundlich models, which are the most well-known models (Gupta et al., 2003). Langmuir's model is based on the principal assumption that the attachment of the adsorbate is only possible if the adsorbent sites are not saturated by monolayer. It is also assumed that all of the vacant sites on the surface of the adsorbent are equivalently sized, similar in shape and uniformly distributed, offering the opportunity of interaction with adsorbates having the same binding energy. In this analysis, the Langmuir model didn't fit the experimental data, which indicates that the adsorption process was not homogenous. Accordingly, negative values of K and Q_o were obtained (Igwe and Abia, 2007). The graph forthe Freundlich model is shown in Fig. 2. K_f and n were calculated from the intercept and slope of the linearized form of the equation, respectively.

The calculated value of K_f was 2.8×10^{-4} ($mg^{1.66}\ g^{-1}{\cdot}L^{-0.66}$) and n was 0.66, which are small but are attributed to a cooperative type of adsorption. As stated by Dada et al. (2012) the value of $n = 1$ indicates that the equilibrium distribution between the solid and liquid phase is independent of the concentration, whereas $1/n > 1$ or $1/n < 1$ shows cooperative and normal adsorption, respectively. The R^2 value for the Freundlich model was 0.85 and for the Langmuir model was 0.77, indicating that the Freundlich model better describes the experimental data, indicating multilayer adsorption.

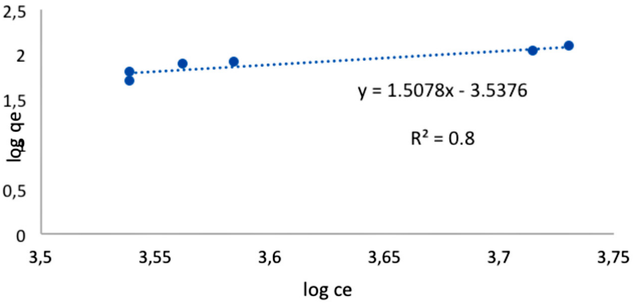

Figure 2

Freundlich plot for COD removal using activated BFA

COD and colour analyses

The factorial matrix, experimental results and corresponding predicted modeling values are shown in Table 4. Removal of COD and colour were carried out simultaneously by adsorption. Optimum conditions for maximum COD removal (61.6%) were adsorbent dose 4 g, pH 8, initial COD concentration 6 000 mg/L, and contact time 4 h, whereas the optimum conditions for maximum melanoidin decolourization (64.0%) were adsorbent dose 4 g, pH 3, initial COD concentration 6 000 g/L, and contact time 4 h. It is practically impossible to maintain the same treatment at different optimum conditions. The single optimum point for the maximum removal of both COD (61.6%) and colour (58.3%) was found at optimum conditions for COD removal.

TABLE 4
Experimental adsorption matrix for COD and colour removal percentage

#	Factors				COD values		Colour removal value	
	X_1	X_2	X_3	X_4	Observed	Predicted	Observed	Predicted
1	1	1	1	1	61.6	*56.1*	58.3	50.9
2	–1	1	1	1	23.2	*20.2*	10.4	19.9
3	1	–1	1	1	36.0	*31.3*	63.4	64.9
4	–1	–1	1	1	25.0	22.6	19.8	33.9
5	1	1	–1	1	52.4	49.5	64.0	51.3
6	–1	1	–1	1	14.0	13.7	61.4	48.2
7	1	–1	–1	1	19.7	24.7	59.1	65.2
8	–1	–1	–1	1	23.2	16.1	60.0	62.1
9	1	1	1	–1	52.4	49.5	54.7	55.8
10	–1	1	1	–1	10.3	13.7	25.6	24.7
11	1	–1	1	–1	27.2	24.7	19.3	41.8
12	–1	–1	1	–1	8.8	16.1	15.8	10.8
13	1	1	–1	–1	44.8	56.1	38.0	27.5
14	–1	1	–1	–1	20.3	20.2	38.1	24.4
15	1	–1	–1	–1	29.2	31.3	14.2	13.5
16	–1	–1	–1	–1	20.3	22.6	3.4	10.5

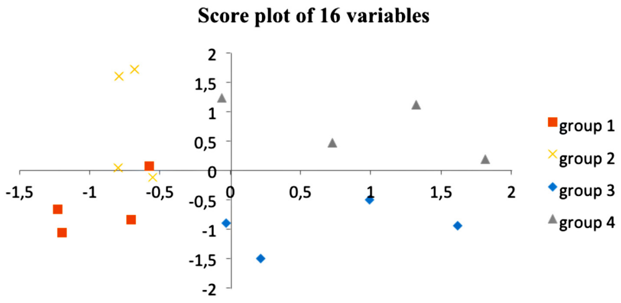

Figure 3
Categorical variables in 4 groups under PCA1 and PCA2

Correlation analysis

During the adsorption process, the relation between adsorption variables was determined using correlation analysis (Table 5). Two- and single-tailed analyses were carried out. Correlation between the variables was generally weak ($r < 0.50$). For some independent variables *r* approached zero. Strong correlation was observed only between initial COD concentration and COD removal, for which the $r = 0.73$, followed by the correlation between the colour removal and contact time for which $r = 0.55$. During single-tailed correlation analyses, all variables had values of $r < 0.50$, which shows weak and positive relations (Table 5).

Principal component analysis (PCA)

In this analysis, PCA was used to identify the major factors that affected colour and COD removal from wastewater, which was revealed by rotated component matrix. The results of the PCA are shown in Table 6. Initial COD concentration and contact time were the main dominant factors for colour and COD removal, respectively. Taking into account the calculated eigenvalues, it was decided to use the first two principal components in this data analysis. The relation of each variable is clearly indicated in Table 6. 59.09% of the total variance was explained by the first and second principal components. Specifically, the first principal component describes 38.41% of total variance and the main contributors were initial COD concentration (0.85), followed by adsorbent dose (0.41). However, the contributions of other variables were low (< 0.50).

TABLE 6
Rotated component matrix of adsorption factors

Factors	**Component**	
	1	**2**
COD removal	0.94	0.02
Colour removal	0.56	0.72
Initial COD concentration	0.85	−0.10
Adsorbent dose	0.41	0.09
pH	0.14	−0.48
Contact time	0.12	0.81

The second principal component accounts for 20.67% of the total variance; contact time (0.81) and pH were the main sources for total variance.

In the PCA analysis only initial COD concentration and contact time were identified as the most influential factors. After the screening, the two factors were analysed and each variable's value was calculated (Fig. 3). The variables were categorized into 4 groups based on the PCA1 and PCA2 results. The results show that the higher the initial COD concentration, the more effective the removal of COD and that the removal efficiency for colour increased with greater contact time and vice versa. Furthermore, these groups were clearly separated by the first and second principal components but the other principal components attribution to variation is limited.

Optimization for COD and colour removal

It was observed that the regression model terms of 3-way and 4-way interactions were insignificant at 95% and neglected in the analysis. According to the regression model output, statistically insignificant terms in the model had no significant impact on COD or colour removal. Hence, only the main effects and the two-way interactions were used to determine the influence on the treatment. The regression analyses were carried out at 95% confidence level and the results are shown in Tables 7 and 8. The regression coefficient of determination (R^2) was used to identify the degree of variability in response that was explained by the linear regression model whereas the *p* values were used to judge whether the results of the main and interaction effects were statistically significant or not. Hence, the results in Table 7 show that the model terms corresponding

TABLE 5
Correlation matrix for dependent and independent variables

		COD removal	**Colour removal**	**Initial COD concentration**	**dose**	**pH**	**Contact time**
Correlation	COD removal	1	0.46	0.73	0.37	0.08	0.17
	Colour removal	0.46	1	0.40	0.28	−0.21	0.55
	Concentration	0.73	0.40	1	0	0	0
	Dose	0.37	0.28	0	1	0	0
	pH	0.08	-0.21	0	0	1	0
	Time	0.17	0.55	0	0	0	1
Sig.(1-tailed)	COD removal		0.04	0.00	0.08	0.38	0.27
	Colour removal	0.04		0.06	0.15	0.22	0.01
	Concentration	0.00	0.06		0.50	0.50	0.50
	Dose	0.08	0.15	0.50		0.50	0.50
	pH	0.38	0.22	0.50	0.50		0.50
	Time	0.27	0.02	0.50	0.50	0.50	

to coefficient values of b_1, b_2, b_5 and b_{10} were statistically significant. The coefficient of determination (R^2) for COD removal was 0.97 and the adjusted R^2 was 0.91, which were indicators of the goodness of fit of the model. This depicted that 97% of the variation in COD removal was explained by the regression model.

The *p* values for significant model terms in Table 7 are between 0.02 and 0.05 and only these terms were used in new regression and incorporated in Eq: 7 below:

$$Y_{COD} = 29.28 + 11.14X_1 + 5.60X_2 + 6.79X_1X_2 + 3.28X_3X_4 \quad (7)$$

where: Y_{COD} is the predicted value of COD removal (%); and X_1 and X_2 are initial COD concentration and adsorbent dose, respectively. X_1X_2 and X_3X_4 were the interaction effects of the initial COD concentration with adsorbent dose and pH with contact time. The sign of the coefficient of regression indicates the direction of the relation and the magnitude of the number shows the degree of influence on COD removal. Generally, variables with a positive coefficient value enhanced COD removal whereas those with negative coefficient values were inversely related to removal. The degree of impact on removal increased with increasing numerical value of the regression coefficient in both cases.

All coefficient values in the regression equation were positive, which shows the enhancement of COD removal. This indicates that COD removal increases as each value of the main and interaction effects increases. The degree of impact on COD removal was in the order of $X_1 > X_1X_2 > X_2 > X_3X_4$. The extent of COD removal was highly influenced by initial COD concentration. Increase in initial COD concentration over the range used increased the removal of COD from 23.2% to 61.6%. Similarly, the interaction effect between initial COD concentration and adsorbent dose also dominated COD treatment. The predicted value of the COD was the function of the main effects (X_1 and X_2) and the 2-way interactions (X_1X_2 and X_3X_4) in the model equation.

TABLE 7
Regression and ANOVA analysis of COD treatment

Coefficients	Coefficient value	SE coefficient	t stat		*P*-value
b_0	29.28	1.166899	25.09		0.000
b_1	11.14	1.166899	9.54		0.000*
b_2	5.60	1.166899	4.80		0.005*
b_3	1.29	1.166899	1.10		0.320
b_4	2.61	1.166899	2.24		0.075
b_5	6.79	1.166899	5.82		0.002*
b_6	2.60	1.166899	2.23		0.076
b_7	-0.60	1.166899	−0.51		0.631
b_8	0.71	1.166899	0.61		0.570
b_9	0.32	1.166899	0.27		0.797
b_{10}	3.28	1.166899	2.81		0.039*
	DF	**SS**	**FS**	**F**	**Significant F**
Regression	10	3656.244	365.6244	16.78219	0.003073
Residual	5	108.9322	21.78645		
Total	15	3765.176			

Statistically significant p values are designated by (*) in the table

TABLE 8
Regression statistical analysis and ANOVA for colour treatment

Coefficients	Coefficients value	Standard error	t Stat	*P*-value	
b_0	37.83	2.40074	15.76	0.000*	
b_1	8.53	2.40074	3.55	0.016*	
b_2	5.98	2.40074	2.49	0.055	
b_3	−4.45	2.40074	−1.85	0.123	
b_4	11.71	2.40074	4.88	0.005*	
b_5	1.40	2.40074	0.58	0.584	
b_6	6.98	2.40074	2.91	0.033*	
b_7	3.13	2.40074	1.31	0.249	
b_8	−2.13	2.40074	−0.89	0.415	
b_9	−6.98	2.40074	−2.91	0.033*	
b_{10}	−7.14	2.40074	−2.97	0.031*	
	DF	**SS**	**FS**	**F**	**Significant F**
Regression	10	6884.522	688.45	7.47	0.0193
Residual	5	461.08	92.22		

For the colour treatment analysis, the coefficient of determination (R^2) was 0.94 and the adjusted R^2 was 0.81, which revealed that the model fits the experimental data well, though less so than the COD model. It was concluded that 94% of the variation in colour removal was explained by the model. Statistically significant terms (Table 8) were used to predict colour removal percentages which are given below.

$$Y_{colour} = 37.83 + 8.53X_1 + 11.71X_4 + 6.98X_1X_3 - 6.98X_2X_4 - 7.14X_3X_4 \qquad (8)$$

where: Y_{colour} is the predicted value of colour removal (%) and X_1, X_4 the initial COD concentration and adsorbent dose, respectively. X_1X_3, X_2X_4 and X_3X_4 were the interactions between initial COD concentration and pH, adsorbent dose and contact time, and pH and contact time, respectively.

All main and interaction effects had positive impacts on colour removal except the interaction between adsorbent dose and contact time, and pH and contact time. The positive values of coefficient terms enhanced the removal of colour and the negative values suppressed colour removal. The degree of impact on colour removal was in the order of $X_4 > X_1 > X_3X_4 > X_1X_3 > X_2X_4$. Moreover, the dominant role for colour removal was played by contact time, followed by initial COD concentration.

CONCLUSION

Simultaneous removal of colour and COD from a melanoidin solution was effectively achieved by batch adsorption using chemically activated BFA. The adsorptive capacity (q_0) was determined to be 124.80 mg/g. BFA is a carbon-rich industrial waste and a good precursor for activated carbon. Characterization of BFA shows that the developed adsorbent was heterogeneous and had irregularly shaped pores, which were responsible for the uptake of different sizes of adsorbate in the adsorption process. In adsorption treatment, adsorbent surface area is important. Accordingly, a surface area of BFA of 160.9 ± 2.8 m^2/g was found to have the capacity to remove pollutants from ethanol distillery wastewater, particularly colour and COD components. Equilibrium isothermal studies showed that the Freundlich model better fitted the experimental data. With the help of a full factorial experimental design, maximum removal of COD was 61.6% at the optimum condition of adsorbent dose 4 g, contact time 4 h, pH 8 and initial COD concentration 6 000 mg/L, whereas colour removal was 64% under the same conditions but at pH 3. The difference in efficiency of COD and colour removal is probably due to variable responses of colour and COD to independent factors. Furthermore, only a few components in the solution might be the cause of colour formation whereas any oxidizeable components will contribute to COD.

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