

## Characterisation and utilisation of fly ash for treatment of brine wastewater in sugar refineries

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### ABSTRACT

In Thailand, sugarcane bagasse is used as a major energy source for power generation, which creates large quantities of fly ash resulting from the combustion of biomass. In this study, the characteristics of fly ash from five bioelectric power plants in Thailand (labelled A, B, C, D and E) was studied and its application for brine water treatment has been tested. Microscopic observations of treated fly ash (TFA) identified carbon as the principal element and revealed a porous structure resulting from the rectangular shape of the plant cells in the precursor material. Furthermore, BET surface area analyses indicated that among all investigated samples, the TFA originating from factories B, C and E exhibited high surface areas (307, 251 and 247 m<sup>2</sup>/g, respectively), while the adsorption isotherms corresponded to those of microporous adsorbents. Consequently, the performance in colour removal from brine wastewater was compared among five TFAs and Norit 1240 Plus, a commercial granular activated carbon used, as reference. The percentages of colour removal from brine wastewater at an adsorption time of 24 h were of 80%, 48%, 85%, 87%, 96% and 96% for TFA from factories A, B, C, D, E and Norit 1240 Plus, respectively, while the maximum dosage for colour removal from brine wastewater using TFA was determined as 12% w/v. Our results suggest that TFA has great prospect for industrial scale application, depending on its chemical and physical characteristics, and may improve the process of brine recycling as well as prevent potential environmental hazards of brine leakage into the soil of agricultural areas.

*Keywords:* Bagasse; Treated fly ash; Brine wastewater; Adsorption; Power plant

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### 1. Introduction

Brine wastewater is the waste water resulting from the regeneration process of the ion exchange resin tower used to remove the colour from the liquor in some sugar refineries. This waste consists of 50 g/L of sodium chloride, natural sugarcane pigments and colourants produced during the raw sugar process. The molar mass of colourants compounds

ranges from 5,000 to 20,000 g/mol [1]. In Thailand, the wastewater decolourisation process in sugar refineries generally involves two steps: carbonation and ion-exchange. Approximately 60%–70% of colourants are removed by carbonation, after which treatment of the resulting brown liquor by adsorption with styrene and acrylic resins packed in an ion-exchange tower yields fine liquor with a colour intensity of less than 200 International Commission for Uniform

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Methods of Sugar Analysis (ICUMSA) units. Regenerating the spent resin with a 10% (m/m) sodium chloride solution for desorption of colourants in conjunction with recycling of the brine effluent by membrane filtration greatly improves the effectiveness of this process. However, several drawbacks of the brine recycling system are still limiting its applicability and need to be addressed. First, the colourants in the brine effluent tend to retard and block the membrane surface. Therefore, the overall process effectiveness is significantly reduced and only 60% reduction in salt consumption can be achieved. In addition, brine effluent storage and potential leakage pose the hazard of severe environmental pollution. In this context, the removal of residual colourants in the brine effluent by bagasse fly ash (BFA), a by-product of bioenergy electric power plants, could emerge as an example of an environmentally friendly and economical practice.

Nowadays, approximately 22% of the biomass power plants in Thailand use bagasse as primary fuel [2], and most of the generated BFA end up as landfill material or plant fertiliser with low economic valorisation. Sugarcane BFA contains 15%–35% (m/m) unburned carbon, which could be activated to serve as a low-cost adsorbent [3].

Researchers from several countries have attempted to develop BFA adsorption systems and used it for different applications in India [4,5], South Africa, Brazil [6] and Thailand [7]. Since it contains 65% (m/m) of fixed carbon, BFA has been used as an adsorbent in the decolourisation of brown sugar liquor. Despite its low surface area of 256 m<sup>2</sup>/g, the high average pore diameter of BFA (3.243 nm) enables it to adsorb medium-sized colourant molecules [7]. Rodríguez-Díaz et al. [6] disclosed a full characterisation of ashes generated by combustion of bagasse from sugarcane ethanol plants in Brazil and Cuba, revealing that ashes from both countries have similar structures and could be applied as adsorbents for both organic and inorganic compounds.

Additionally, BFA has been studied for a wide range of similar applications, such as dye adsorption [2,8–10], heavy metal removal [4,8], adsorption of phenolic compounds [5,11], removal of volatile organic compounds [12] and removal of organic matter (COD) from wastewater of molasses produced in distillery plants [13]. Wong et al. [14] reported a good colour adsorption capacity in the range of 87.3%–94.74% using activated carbon from BFA. However, reports describing the application of BFA to adsorb colourants in brine solution have yet remained elusive to the best of our knowledge. In addition, the elimination of metal ion in wastewater by adsorption techniques has gained attention worldwide and has been reviewed intensively elsewhere [15–17]. As a result, this study is focused on the evaluation of treated fly ash (TFA) in the treatment of spent brine water, as well as the distribution of metal ions in brine wastewater treated by TFA. The detailed physicochemical properties and adsorption capacity of fly ash collected from five different bioenergy plants in Thailand before and after treatment are presented and discussed.

## 2. Materials and methods

### 2.1. Sampling and preparation of fly ash

Fly ash was collected from five power plants (coded as A, B, C, D, E) located in the central and northeast provinces

of Thailand between May and June 2017. In Table 1, the measured proportion of bagasse in the total biomass used as fuel is given for each power plant. The BFA samples were collected either from the waste scrubber, waste pond or clarifier system of the boiler by sieving through a 600 µm mesh. Portions of the samples were analysed as “untreated fly ash (UNTFA)”, while the remaining material was subjected to additional treatment steps as follows: first, sand and dirt were separated from the samples by floatation in water before the bagasse ashes were washed with water until a pH of 7.0–7.2 was achieved. The ashes were dried in an oven at 120°C until completely dried and then stored in sealed plastic bags for further use.

### 2.2. Physical and chemical characterisation of fly ash

In order to determine the particle size distribution, 50 g of TFA were analysed following the applied standard test method (ASTM) D2862-10 [18]. Determination of the surface area and pore properties of the TFA samples was conducted by recording nitrogen adsorption isotherms via the Brunauer–Emmett–Teller (BET) method using ASAP2010 equipment (Micromeritics, USA). The specific surface area, micropore volume, total pore volume and the average pore size were calculated as described by Ngernyen et al. [19]. Moisture content, total organic matter and total inorganic matter in UNTFA and TFA were determined according to ASTM 2974-87 [20,21] using a Carbolite Gero Furnaces Model ELF (Carbolite Gero, UK). The weight loss after burning, which is known as the loss on ignition (LOI), was analysed for 1.0 g of TFA according to the ASTM-D7348-80 [21,22]. This method is generally accepted for estimating the unburned carbon content of fly ash [21]. Specifically, the samples were burned at 750°C for 2 h, and weighed after cooling down in a desiccator [21]. All analyses were carried out in triplicate. The pH of UNTFA, TFA and Norit 1240 Plus (reference GAC) was measured in accordance to ASTM-D3838-80 [23,24]. The iodine number, a relative indicator of porosity in activated carbon, was calculated by the mass (mg) of adsorbed iodine from a standard 0.05 M iodine solution for TFA samples and Norit 1240 Plus, following the standard test method, ASTM D4607-86 [25,26].

The chemical composition of UNTFA and TFA from five factories was analysed by X-ray fluorescence spectroscopy. The contents were determined and expressed as percentage (m/m) of their oxide forms via semi-quantitative analysis using an AXIOS MAX X-ray fluorescence spectrometer (Application Omnia) as described by Rodríguez-Díaz et al. [6].

Table 1  
Feed fuel and source of biomass for co-generation

Ash sample source	Bagasse (% m/m)	Others <sup>a</sup> (% m/m)
Factory A	86	14
Factory B	100	0
Factory C	95	5
Factory D	68	32
Factory E	70	30

<sup>a</sup>Rice husk, eucalyptus chip, woodchip, sugarcane leaf.

Fourier transform infrared spectroscopy (FTIR) Bruker/Tensor 27-Hyperion (USA) was used to examine the presence of specific functional groups in the TFA samples over a range of 400–4,000  $\text{cm}^{-1}$  [6]. The microscopic structure of TFA samples was investigated via scanning electronic microscopy (SEM) using a JEOL JSM-6010LV microscope (JEOL, USA) coupled to an X-MaxN Oxford Instruments X-ray energy dispersive spectrometer (EDX) (UK) [6]. The elemental composition of the TFA samples was measured by analysing the EDX spectrum generated by a spot analysis method. The average diameter of TFA particles was determined by sampling the SEM images at random locations ( $n = 150$ ) using the ImageJ analysis software (NIH, USA).

### 2.3. Colour adsorption by fly ash

The effectiveness of colour adsorption by fly ash in brine wastewater was analysed according to a method adapted from Ngernyen et al. [19] with minor modifications. In brief, TFA samples were dehydrated in an oven at 120°C during 3 h before analysis. Then, 2.5, 5.0 and 6.0 g of TFA (5%, 10% and 12 w/v) were immersed in 50 mL of brine wastewater for 24 h and subsequently separated by filtration using a filter membrane (0.45  $\mu\text{m}$ ). The percentage of colour removal from the wastewater was calculated by measuring the absorbance of wastewater samples in an ultraviolet (UV)–spectrophotometer (Helios-Alpha, Thermo Spectronic, USA) at  $\lambda_{\text{max}}$  of 420 nm and compared with the blank value of the untreated brine wastewater. The percentage of colour removal was calculated as follows:

$$\% \text{Removal} = \left( \frac{\text{Abs}_0 - \text{Abs}_t}{\text{Abs}_0} \right) \times 100 \quad (1)$$

where  $\text{Abs}_0$  is the initial absorbance of the wastewater, and  $\text{Abs}_t$  is the absorbance of wastewater at 24 h. The pH and conductivity of the ashes were measured after the colour removal treatment. All adsorption tests were carried out in triplicate.

### 2.4. Breakthrough studies of colour removal in column adsorption

The decolourisation of brine wastewater by TFA was performed using Millipore 5-cm-diameter and 23-cm-height Vantage VL44 columns (Billerica, MA, USA). The equipment was set up as shown in Fig. 1. Five centimeters of sand was placed into the base of the column before packing 40 g of TFA downwards. Then, brine wastewater was continuously pumped through the packed column while the pressure of diaphragm pump was maintained at 30 stocks (around 5 mL/min). Wastewater samples were collected before and after treatment and analysed in order to evaluate the decolourisation efficiency of TFA. The brine wastewater flow was stopped when the colour removal efficiency dropped below 50%.

### 2.5. Statistical analyses

Analysis of variance (ANOVA) was performed to identify significant differences between mean values of surface area, average pore size and proportion of mesopores in TFA.

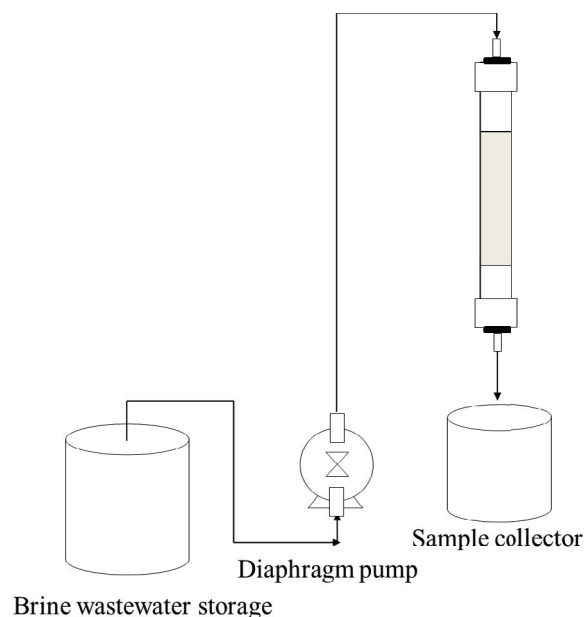


Fig. 1. Schematic overview of the fixed-bed experiment setup.

## 3. Results and discussion

### 3.1. Physical properties

The measured physical properties of UNTFA and TFAs comprised particle size distribution (PSD), bulk density, surface area and pore diameter. The PSD of TFA from different locations displayed in Fig. 2 indicates that the TFA from factories A, D and E is characterised by a normal distribution of particle size, with most particles in the range of 890–1,785  $\mu\text{m}$  accounting for 64% of the total weight (Fig. 2a). The PSDs for factories B and C (using fuel containing more than 95% bagasse) had most particles in the range of 384–1,785  $\mu\text{m}$  (76% w/w) (Fig. 2b). Notably, a normal PSD facilitates packing of the material in the reactor column and aids in preventing critical pressure drops [6,27].

Adsorption and desorption isotherms of  $\text{N}_2$  at  $-196^\circ\text{C}$  of TFAs are shown in Fig. 3. The isotherms of all TFA samples were found to correspond to Type 1 under the Brunauer–Deming–Deming–Teller (BDDT) classification [28]. This type of isotherm indicates that the adsorbent is a microporous substance [29].

The isotherms were used to calculate the pore properties: surface area, pore volume, pore diameter and average pore size of the TFAs and UNTFAs, which are shown in Table 2 along with that of Norit 1240 Plus, an activated carbon reference standard. According to Bansode [30], a higher total surface area of TFA is anticipated to increase adsorption. Similarly, a high pore volume in conjunction with a combination of large and small pores is supposed to greatly benefit the adsorption of sugar colourants [31]. The results of the total surface area determination for five samples show that TFA from factories B, C and E presented the highest surface areas with 307, 251 and 247  $\text{m}^2/\text{g}$ , respectively, and were grouped together by the ANOVA. In addition, the statistical analysis of total pore volume and proportion of mesopores indicated that TFA from factory B had the

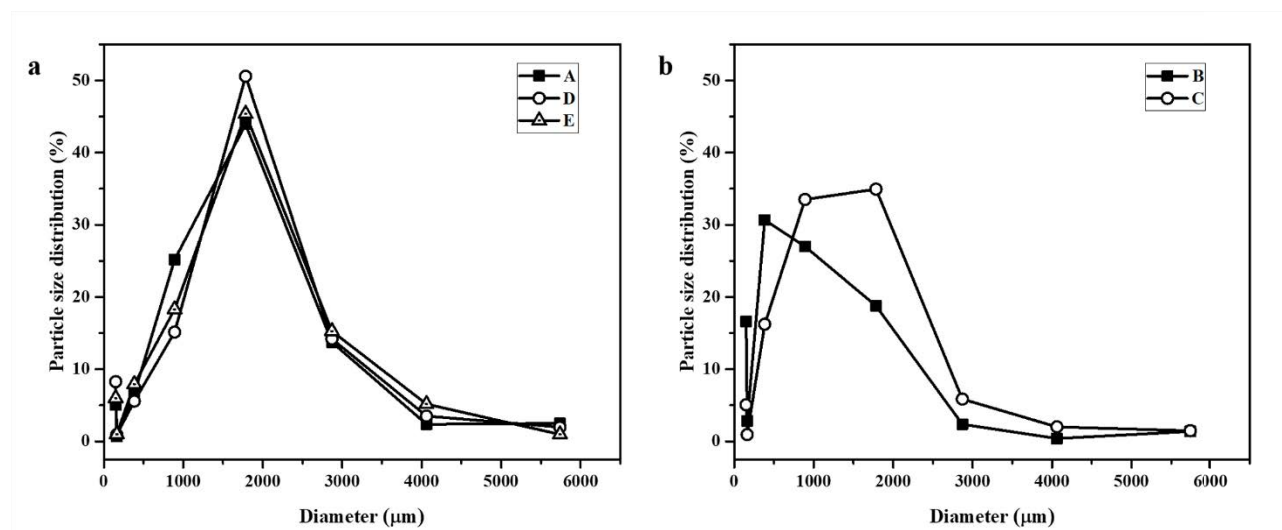


Fig. 2. Particle size distribution (PSD) for the TFA from factories A-E.

Table 2

Surface area ( $S_{\text{BET}}$ ), micropore volume ( $V_{\text{mic}}$ ), total pore volume ( $V_{\text{T}}$ ) and average pore size ( $D_{\text{p}}$ ) for TFA from different sources

TFA sources	$S_{\text{BET}}$ (m <sup>2</sup> /g)	$V_{\text{mic}}$ (cm <sup>3</sup> /g)	$V_{\text{T}}$ (cm <sup>3</sup> /g)	$D_{\text{p}}$ (nm)	Mesopore proportion (%)	Iodine number (mg/g)
Factory A	167 <sup>b,*</sup>	0.040	0.118 <sup>b</sup>	2.95 <sup>b,*</sup>	69 <sup>b,*</sup>	239
Factory B	307 <sup>c</sup>	0.110	0.176 <sup>c</sup>	2.29 <sup>a</sup>	38 <sup>a</sup>	148
Factory C	251 <sup>c</sup>	0.080	0.152 <sup>bc</sup>	2.42 <sup>a</sup>	48 <sup>a</sup>	259
Factory D	37 <sup>a</sup>	0.008	0.033 <sup>a</sup>	3.59 <sup>c</sup>	76 <sup>b</sup>	318
Factory E	247 <sup>c</sup>	0.083	0.150 <sup>bc</sup>	2.43 <sup>a</sup>	45 <sup>a</sup>	260
Norit 1240 Plus <sup>‡</sup>	248	0.017	0.298	4.80	94	945

<sup>‡</sup>Activated carbon for comparison with fly ash.

\*Means with the same letters in the same column do not show statistically significant difference at the 95% confidence level ( $p < 0.05$ ) by Duncan's new multiple range test (DMST) which *a* is the lowest and *c* is the highest value at the same column.

highest total pore volume, albeit with the lowest proportion of mesopores. This result could be explained by a different combustion technology and primary material used as fuel (100% bagasse) at factory B.

### 3.2. Chemical properties

The chemical properties of ash samples from the five power plants were either analysed directly (UNTFA) or after being washed and dried (TFA) to remove sandy impurities and other types of dirt. As a result, the moisture content in the TFA samples was generally lower than that found in UNTFA, as shown in Table 3. The LOI is commonly used to estimate the percentage of combustible carbon in the material. Since washing can remove some decomposable organic compounds, UNTFA samples from all factories displayed lower LOIs than those found in the corresponding TFA samples. Specifically, the UNTFAs from factories B and C had similar LOIs, at 50.7% (m/m), while TFA samples of both factories had a greater LOI content of 78.4% (m/m). However, the LOIs of TFA and UNTFA from factories A and E were greater than 90% (m/m), which might be related to local

differences in combustion technology and boiler feed management. However, these LOI values are higher than that of the floating ashes reported by Montakarnitwong et al. [32] (~20.4% of LOI), who studied BFA from a Thai sugar mill. In addition, other possible reactions, such as calcination of inorganic carbonates, desorption of physically and chemically bound water and oxidation of iron minerals, have to be accounted in this analysis [21] as a potential cause of overestimation of LOI carbon. Consequently, total inorganic matter (TIM) was analysed in UNTFA and TFA. Samples of UNTFA from factories A–E displayed TIM concentrations of 9%, 49%, 12%, 22% and 15% (m/m), respectively. Considering the data of TIM in Table 3, only TFA from factories B and E displayed a remarkable decrease compared with UNTFA, whereas samples from factories A and D displayed an increase of TIM. In case of factory C, no influence on TIM by the treatment could be measured. Notably, these findings represent advantageous properties regarding the use as colour adsorbent, which typically benefits from low levels of inorganic matter. The TIM was found to be related to silicates (SiO<sub>2</sub>) and sodium oxide (Na<sub>2</sub>O), of which high contents were found in the samples from factories B and D. Fly ashes

from all factories showed contents of inorganic compounds (e.g.,  $\text{SiO}_2$ ), which are comparable with those given in the literature [6]. The differences observed in this study could be attributed to many different factors such as the soil mineralogy, moisture content, harvesting procedure, biomass composition, combustion process or mill characteristics [6].

FTIR spectra for TFA from five factories are shown in Fig. 4. The weak peaks between 2,897 and 2,984  $\text{cm}^{-1}$  in TFA of factories B and C may be attributed to organic OH groups [33] and the weak band at 2,900  $\text{cm}^{-1}$  to C–H aliphatic axial deformation in  $\text{CH}_2$  and  $\text{CH}_3$  groups [34]. The valley observed at 1,566  $\text{cm}^{-1}$  is assigned to the asymmetric

stretching vibration of  $\text{NO}_2$  [35]. The FTIR spectra of TFA from factories A, D and E show a peak at approximately 1,437  $\text{cm}^{-1}$ , which may be caused by C=C stretching vibrations [6]. The strongest signals in TFA from all factories is observed in the 950–1,250  $\text{cm}^{-1}$  region and relates to (alumina) silicates and silica polymorphs due to –O–Si–O– and –O–Al–O– stretching modes [36], which is in good agreement with results from XRF measurement (data not shown). The band at 870  $\text{cm}^{-1}$  can be assigned to Si–OH bonds or Al–OH bonds [37]. The strong signal at 469  $\text{cm}^{-1}$  of TFA from factories A, B and C (which use a high volume of non-bagasse fuel) is assigned to the Si–O bending mode [36].

Table 3  
Chemical and physical properties of TFA from factories A–E

TFA sources		Moisture (% m/m)	LOI (% m/m)	TOM (% m/m)	TIM (% m/m)	pH	$\text{SiO}_2$ (%TIM)	$\text{Na}_2\text{O}$ (%TIM)
Factory A	UNTFA	9.9	91.5	81.8	8.3	7.2	5.6	0.4
	TFA	0.7	92.2	85.8	13.5	7.2	4.8	0.6
Factory B	UNTFA	5.9	50.7	45.0	49.1	7.9	7.2	3.6
	TFA	0.7	78.4	74.5	24.8	7.8	10.5	1.2
Factory C	UNTFA	11.6	50.7	76.9	11.5	7.9	4.4	1.1
	TFA	2.4	78.4	86.2	11.4	7.8	4.5	0.3
Factory D	UNTFA	17.5	40.3	60.5	22.0	8.2	11.0	1.2
	TFA	2.7	84.3	70.6	26.7	7.2	4.6	1.1
Factory E	UNTFA	4.9	89.5	79.3	15.8	8.4	7.6	1.0
	TFA	3.4	91.7	84.4	12.2	8.3	2.3	0.1

TOM, total organic matter; TIM, total inorganic matter.

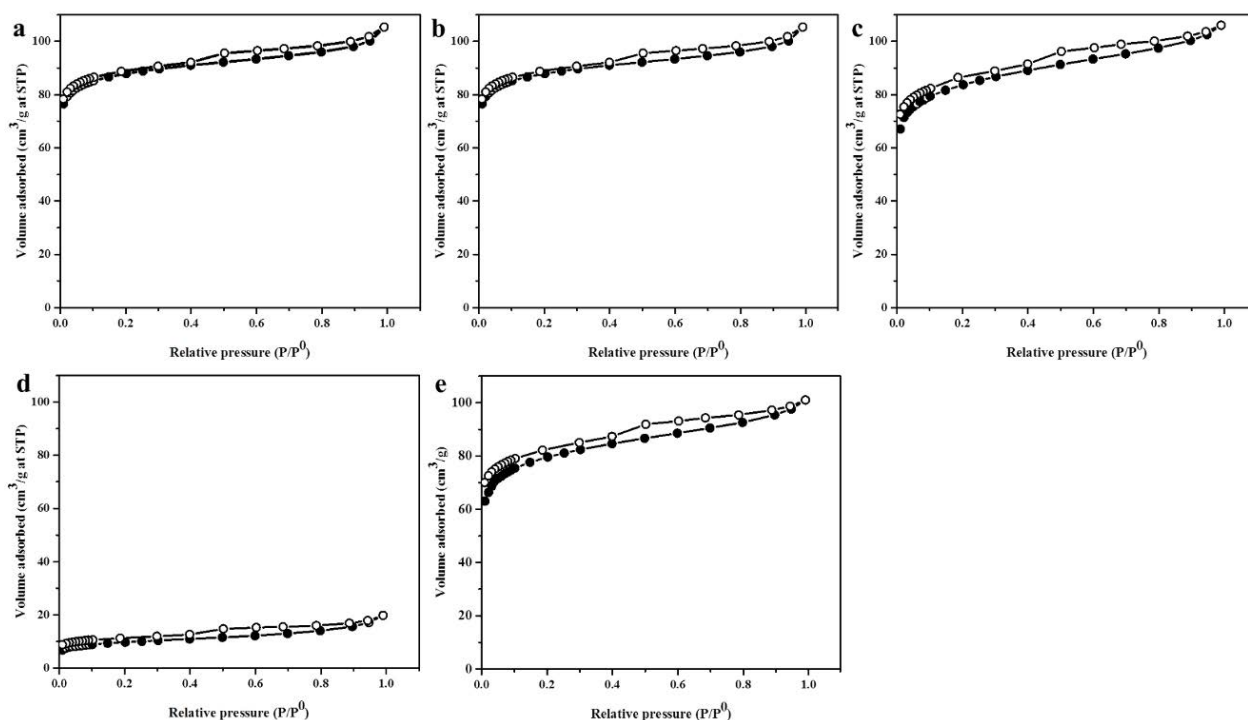


Fig. 3.  $\text{N}_2$  adsorption–desorption isotherm for TFA at 77 K: (a) factory-A; (b) factory-B; (c) factory-C; (d) factory-D; (e) factory-E. The corresponding open symbols indicate desorption data.

This interpretation correlates with the elemental analysis described in Table 4. The functional group analyses of TFA from all factories yielded largely similar results, indicating that the TFAs roughly comprise the same types and quantities of functional groups. This may explain similar adsorption properties of TFA between factories.

Microscopic observations (SEM) of the porosity and structure in TFA from factories A–E, presented in Figs. 5–9. Figs. 5a, 6a, 7a, 8a and 9a show that the plant cell remnants in all fly ash samples have similar rectangular structural characteristics. This may be explained by conservation of the cellular structure of the sugarcane fibres, since the fly ash was obtained from power plants using primarily bagasse (more than 95%) as the fuel. All TFA samples are characterised by pronounced porosity (Figs. 5b, 6b, 7b, 8b and 9b) and present linear and skeletal shapes with holes and threads in each fold [6]. The pores visible in Figs. 5c, 6c, 7c, 8c and 9c were measured to have an average diameter of 7.8, 5.7, 11.9, 10.7 and 10.4  $\mu\text{m}$ , respectively.

An EDX was used to detect the elemental components of TFA samples from the five power plants. The main elements found were carbon, oxygen, silica and calcium. All TFA spectra contained more than 73% of carbon and 10% of oxygen (Table 4). This ratio appears to result from the epidermal layer of biomass fibres covered by siliceous matter and oxygen [6]. The high carbon content measured by EDX positively correlate with the LOI measurements (Table 3). When the carbon content measured by EDX increased, the LOI value increased as well.

### 3.3. Adsorption effectiveness in brine wastewater

The optimal dosage for colour removal from brine wastewater by TFA was investigated, and the results are compiled in Fig. 10. Expectedly, the percentages of colour removal increased with increasing amount of TFA for the same adsorption time. Comparing the figures, it can be noted that for both Norit and TFA the equilibrium was reached after the same time of treatment. However, Norit requires a much lower amount (2.5 g) compared with TFA (6 g) to reach the equilibrium.

The percentages of colour removal in brine wastewater after 24 h were 80%, 48%, 85%, 87% and 96% for TFA from factories A, B, C, D and E, respectively. In this study, the target percentage of colour removal was defined as 50%, corresponding to a light brown colour appearance. Hence, the TFAs from all factories were found adequate for adsorbing the colour in brine wastewater to the desired threshold, with the exception of TFA from factory B. In the latter case, the low activity can presumably be attributed to the low proportion of mesopores (37%) compared with TFAs from factories C and E (47% and 45%, respectively). This assumption is corroborated by the fact that co-generation using various biomass sources in different ratios is likely to alter the ash properties and adsorption efficiencies compared with fly ash from pure bagasse. Moreover, the colour removal percentage of TFA from different factories was linearly correlated with the iodine number ( $R^2 = 0.76$ ), providing strong indication for the colour adsorption to take place in the micropores of the TFA. The pH of the initial brine wastewater was increased within 3 h from 4.7 to

Table 4  
Elemental components of TFA from factories A–E

Elements	Factories (weight, %)				
	A	B	C	D	E
C	80.6	75.9	88.0	83.7	73.3
O	14.3	18.7	10.0	13.9	15.4
Si	1.5	3.3	0.7	0.2	0.9
Ca	1.2	–	0.7	1.8	9.9
Fe	0.9	–	–	–	–
S	0.3	–	–	0.2	0.5
Al	0.3	–	–	–	–
Mg	0.3	0.5	0.3	0.2	–
P	0.2	0.3	0.3	–	–
K	0.2	–	–	–	–

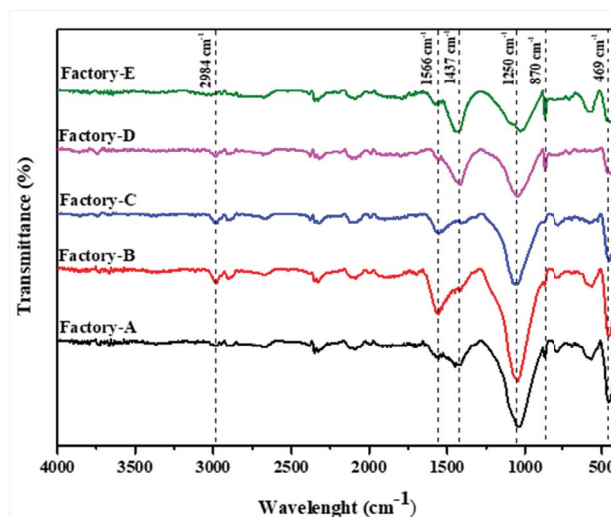


Fig. 4. FTIR spectrograms of TFA from factories A–E.

7.5 and remained stable at approximately 7.4–7.6 (data not shown) due to the transferring of  $\text{K}^+$  or  $\text{Ca}^{2+}$  ions from the ash to the solution [7]. A maximum dosage of 6.0 g and an adsorption time of 6 h were used to compare the effectiveness of different TFA for colour removal in brine wastewater. Apart from the adsorption of colourants from brine solutions, the removal of heavy metal ion contaminants in wastewater has gained considerable attention in the recent years [15–17]. Therefore, we also analyzed the concentration of commonly found metal ions in brine wastewater before and after colour adsorption using inductive coupled plasma spectroscopy (ICP). The ICP results show that while fly ash treatment (Table S1) did not result in removal of chromium, iron, manganese and zinc ions, the concentration of mercury, calcium, potassium, magnesium, sodium and chloride in brine wastewater was reduced by 42%, 32%, 11%, 17%, 0.5% and 12%, respectively. This further indicates no dissociation of heavy metal ions from fly ash into the brine solution occurs. With respect to the potential dissociation of BFA into the brine wastewater, the conductivity, turbidity,

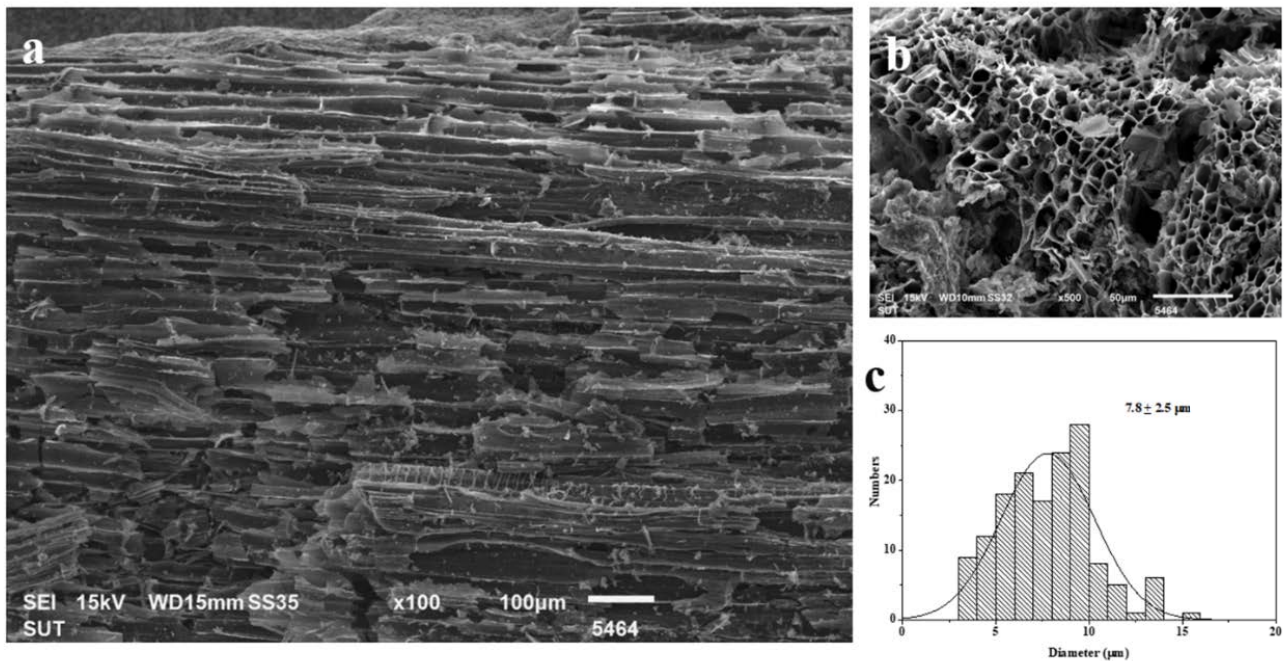


Fig. 5. SEM of TFA from factory A; (a) cell structure in TFA, (b) pores visible in TFA and (c) average diameter of TFA.

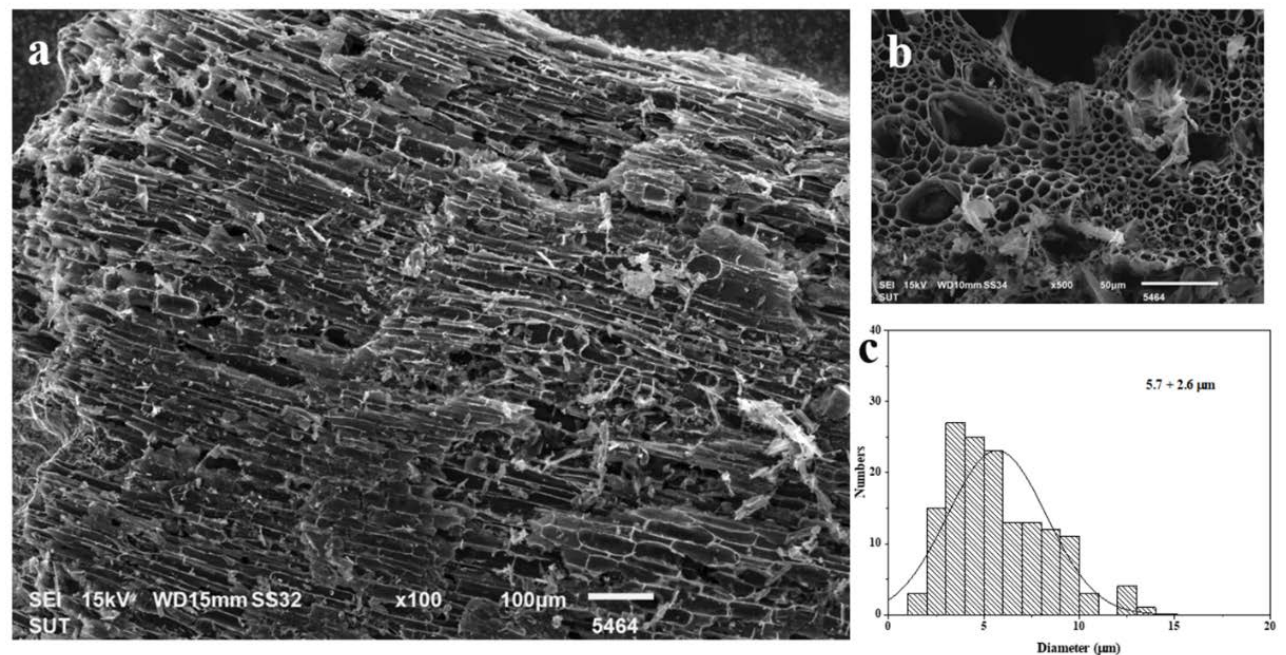


Fig. 6. SEM of TFA from factory B; (a) cell structure in TFA, (b) pores visible in TFA and (c) average diameter of TFA.

chemical oxygen demand (COD), %Brix and total solid content were compared between original brine wastewater and fly ash-treated wastewater at the optimal dose (6 g) and adsorption time (6 h), as shown in Table S2. The conductivity, COD and %Brix decreased compared with untreated brine wastewater. However, the small increase of turbidity and total solid may indicate the release of some fine carbon

particles from the fly ash into the treated brine sample. On an industrial scale, the adsorption of wastewater with fly ash should, therefore, be coupled with membrane filtration to remove these fine particles from the treated wastewater before recycling. In the case, a better filtration of metal ions is necessary, Metal organic framework based materials could be a better option as proposed in Li et al. [16].

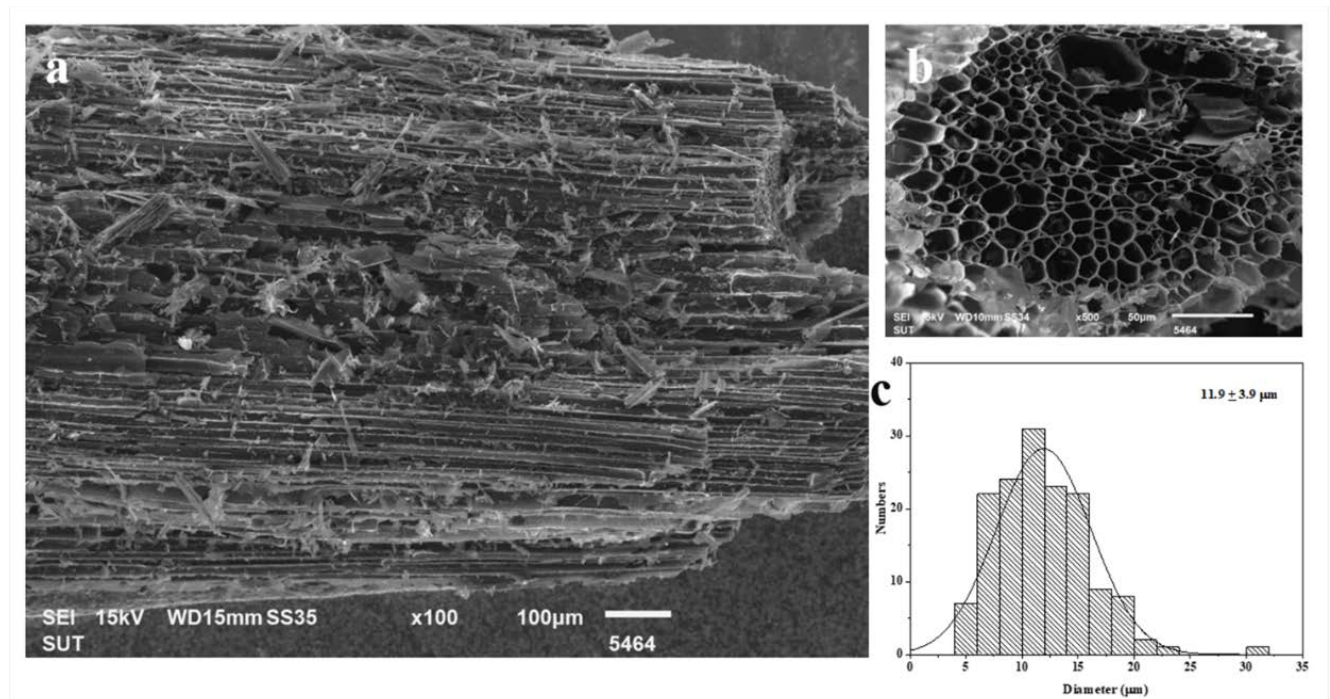


Fig. 7. SEM of TFA from factory C; (a) cell structure in TFA, (b) pores visible in TFA and (c) average diameter of TFA.

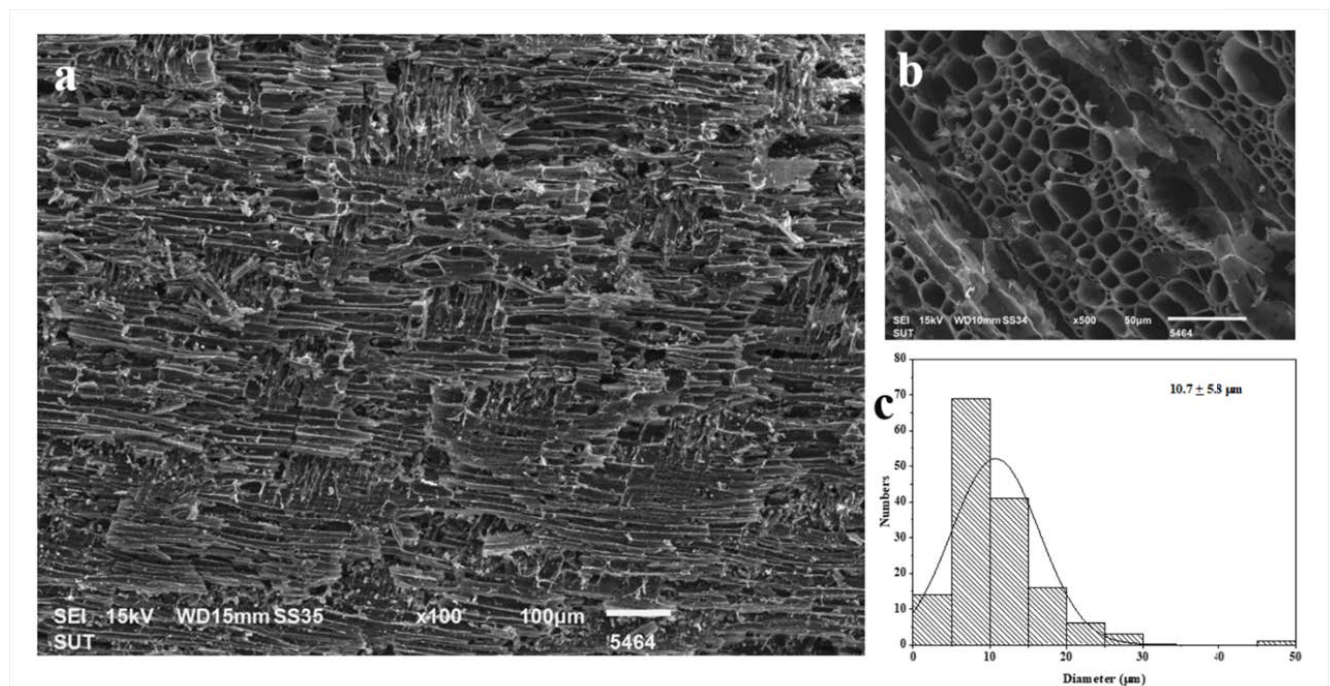


Fig. 8. SEM of TFA from factory D; (a) cell structure in TFA, (b) pores visible in TFA and (c) average diameter of TFA.

The comparison between the adsorption efficiency of TFA and Norit 1240 Plus (Fig. 11) at the optimal dose (6 g) and adsorption time (6 h) revealed the same effectiveness found in previous experiments. The percentages of colour removal were 83%, 44%, 84%, 89%, 94% and 96% for TFA from factories A, B, C, D, E and Norit 1240 (GAC), respectively. TFA

from factory E (70% bagasse), characterised by a high carbon content (LOI) similar to TFA from factory A, was found to show the highest adsorption efficiency. However, the surface area ( $S_{\text{BET}}$ ) of TFA from factory E was higher than that found in the TFA of factory A, which could explain the greater adsorption capacity.



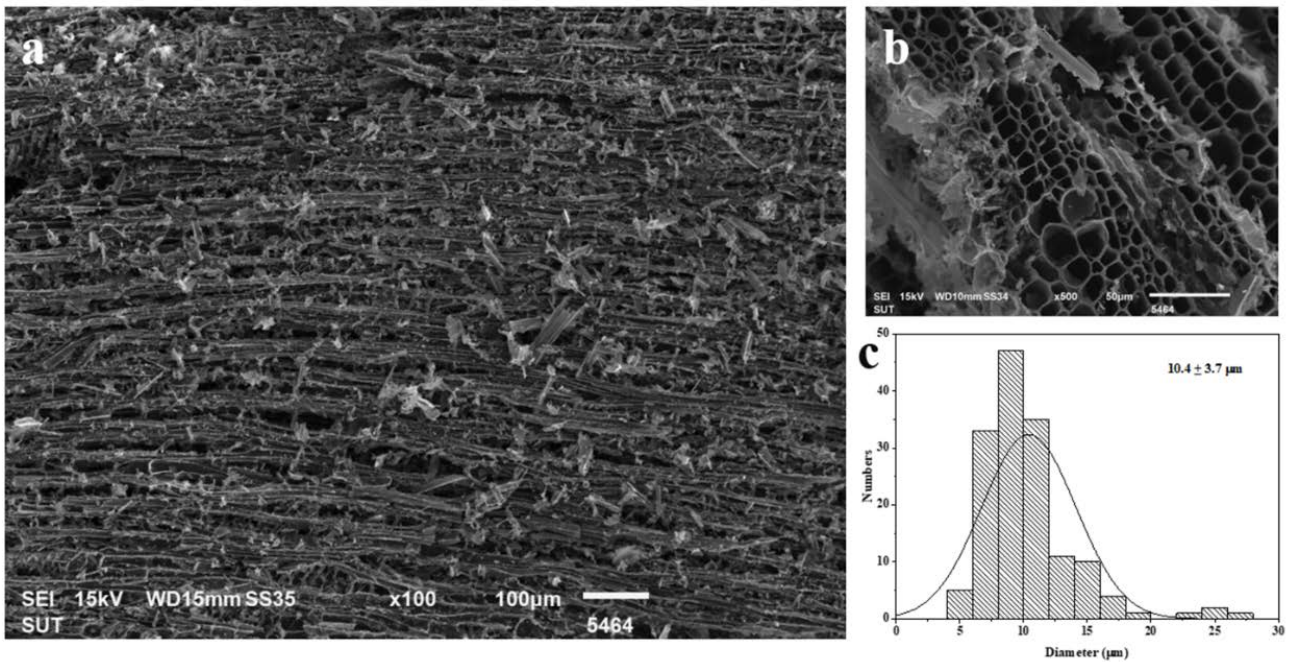


Fig. 9. SEM of TFA from factory E; (a) cell structure in TFA, (b) pores visible in TFA and (c) average diameter of TFA.

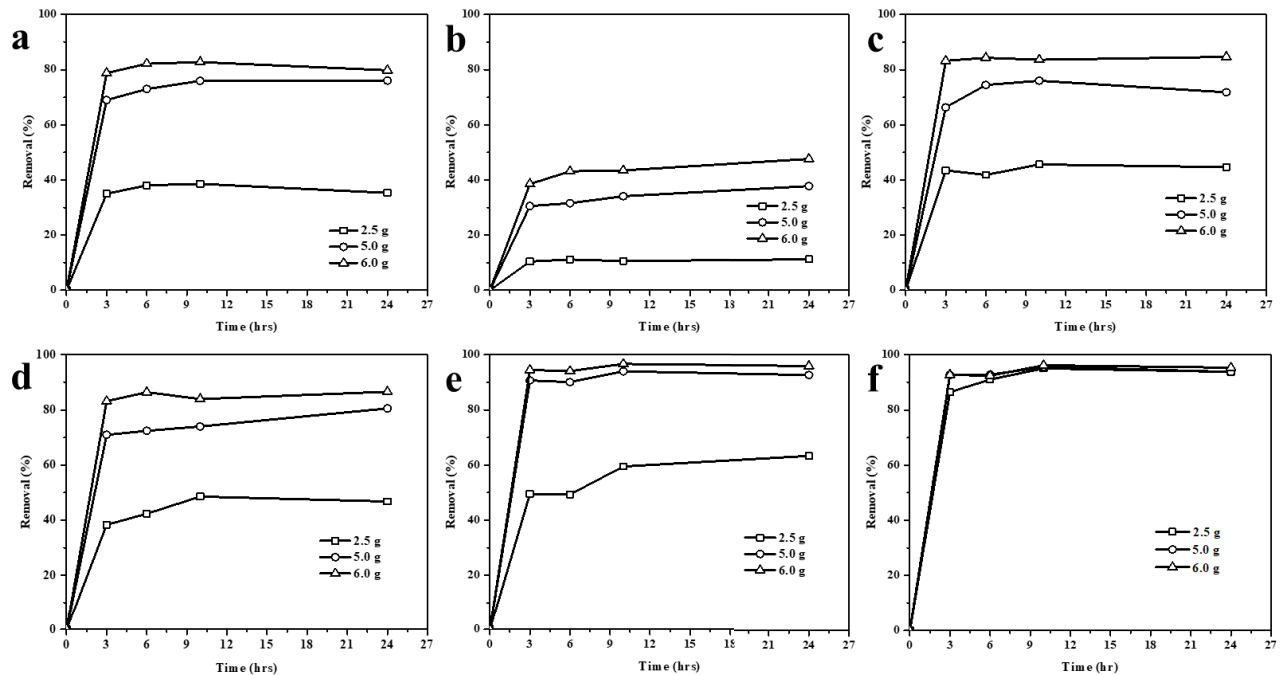


Fig. 10. Colour removal from brine wastewater by TFA from factory A (a), factory B (b), factory C (c), factory D (d), factory E (e) and Norite 1240 (f) at room temperature using doses of 2.5, 5.0 and 6.0 g, adsorption times between 0 and 24 h, and wastewater volume of 50 mL.

3.4. Breakthrough test

The objective of the breakthrough study conducted in this work was to perform a preliminary assessment of the applicability of TFA as adsorbent in an industrial-scale fixed

bed column. Breakthrough curves of TFA from factories A–E on colour removal from brine water are displayed in Fig. 12. The results show that the required effluent volumes for fixed bed columns loaded with 40.0 g TFA to achieve a colour reduction of at least 50% (colour in effluent left OD420 nm ~0.7)

are about 405, 44, 330, 260 and 425 mL for TFA from factories A, B, C, D and E, respectively. Applying these results on the brine wastewater stream from the sugar refinery process, it is anticipated that using approximately 94 kg TFA from factory E would suffice to reduce the colouration in 1 m<sup>3</sup> brine wastewater to 50% of the initial value.

#### 4. Conclusion

The physical and chemical characterisation of TFA obtained from different sources revealed high carbon

content and porosity for all samples, which constitute key properties for a potential application of TFA as adsorbent material. Notably, the percentages of colour removal from brine wastewater achieved using TFA were comparable with those obtained via commercial activated carbon, suggesting the possibility of applying low-cost BFA as a potent adsorbent for wastewater colourants in sugar factories. Hence, the additional valorisation potential for fly ash in brine wastewater management is deemed to provide important economic and ecologic benefits promoting the reuse of this abundant by-product of co-generation. Only minimal treatment of fly ash by washing with water is required before application, and the variation of bagasse content in biomass utilised by bioenergy plants is of little concern since no direct correlation of variety and adsorption capacity was found in this research. Additionally, this study demonstrates the feasibility and prospect of TFA-based colourant adsorption for improving the process of brine recycling and overcoming the environmental problems associated with brine leakage into the soil and agricultural areas. Further studies should be conducted on operational costs for pilot- or industrial-scale applications.

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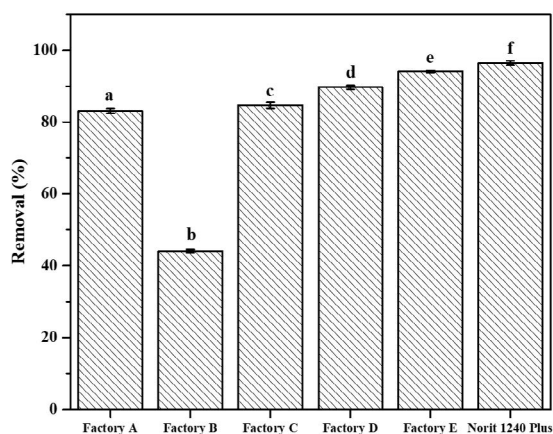


Fig. 11. Comparison of the percentage of colour removal from brine wastewater between using TFA and granular activated carbon (Norit 1240) at room temperature applying 6.0 g of adsorbent, an adsorption time of 6 h and a 50-mL volume of brine wastewater. The data represent mean  $\pm$  standard deviation of three replicate samples from one experiment. Bars with different letters are significantly different ( $p < 0.05$ ).

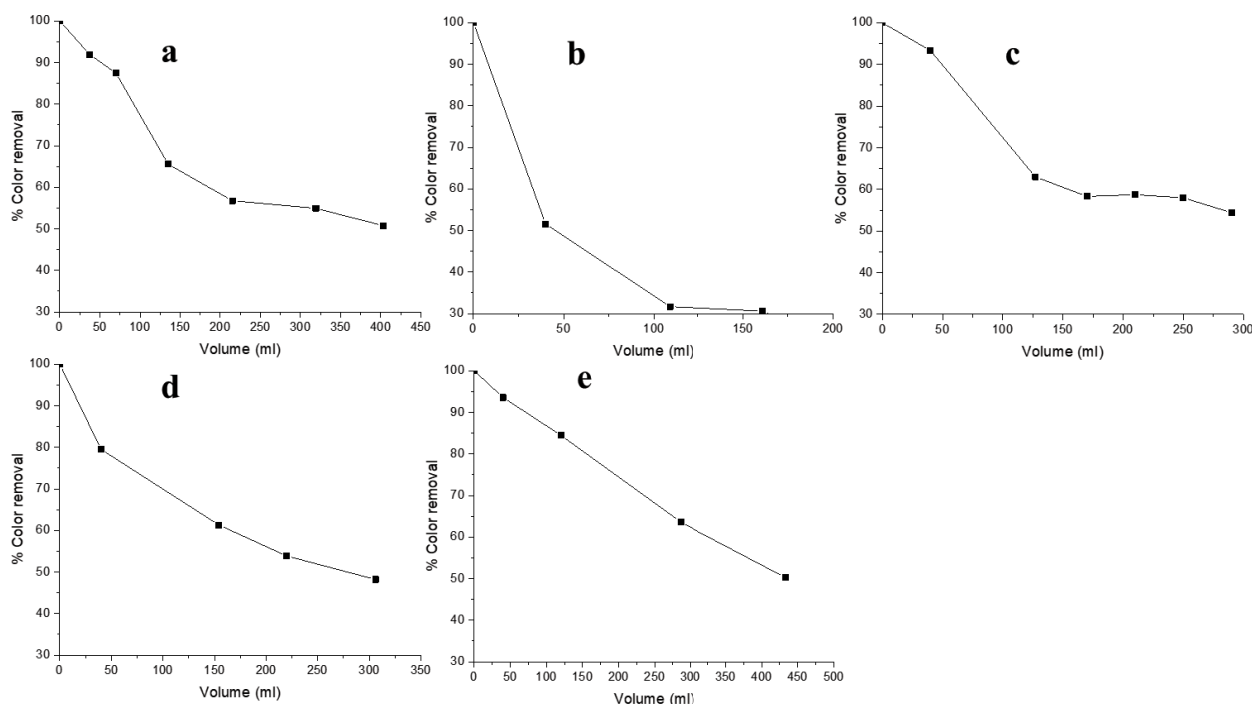


Fig. 12. Breakthrough curves for colour removal from brine wastewater by TFA from factories A–E.

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## Compliance with ethical standards

## Conflict of interest

All authors of this research paper declare that they have no conflict of interest.

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**Supplementary information:**

Table S1

Metal ions contained in brine wastewater before and after adsorption at room temperature using 6.0 g of treated fly ash from factory A, an adsorption time of 6 h and a 50 mL volume of brine wastewater

	As (mg/L)	Cr (mg/L)	Cu (mg/L)	Fe (mg/L)	Hg (mg/L)	Mn (mg/L)	Pb (mg/L)	Zn (mg/L)	Ca (mg/L)	K (mg/L)	Mg (mg/L)	Na (mg/L)	Cl (mg/L)
Brine before	0.00	22.9 ± 0.3	0.00	25.9 ± 1.2	5.2 ± 0.8	4.8 ± 0.2	0.00	1.7 ± 0.2	239 ± 128 <sup>a,*</sup>	225 ± 2 <sup>a,*</sup>	48 ± 14 <sup>a,*</sup>	6,516 ± 52	14,613 ± 284
Brine after	0.00	22.5 ± 0.2	0.00	25.9 ± 1.1	3.0 ± 0.9	4.6 ± 0.2	0.00	1.6 ± 0.0	161 ± 128 <sup>b</sup>	201 ± 23 <sup>b</sup>	40 ± 14 <sup>b</sup>	6,484 ± 44	12,877 ± 946

The data represent mean ± standard deviation of three replicate samples from one experiment.

<sup>a</sup>Statistical significance assumed at 95% confidence level from *t*-test of paired samples for means.

Table S2

Brine wastewater characteristics before and after adsorption at room temperature using 6.0 g of treated fly ash from factory A, an adsorption time of 6 h and a 50 mL volume of brine wastewater

	pH	EC (µS)	Turbidity (%)	COD (mg/L)	% Brix	Total solid (mg/L)
Brine before	6.3 ± 0.0 <sup>a,*</sup>	29.83 ± 0.40	0.27 ± 0.03 <sup>a,*</sup>	9,096 ± 902 <sup>a,*</sup>	2.78 ± 0.01	35,000 ± 1,000
Brine after	7.9 ± 0.1 <sup>b</sup>	29.37 ± 0.06	0.43 ± 0.01 <sup>b</sup>	4,910 ± 374 <sup>b</sup>	2.64 ± 0.04	37,333 ± 7,234

The data represent mean ± standard deviation of three replicate samples from one experiment.

<sup>a</sup>Statistical significance assumed at 95% confidence level from *t*-test of paired samples for means.