Comparative and Optimization Studies of Adsorptive Strengths of Activated Carbons Produced from Steam- and CO₂-Activation for BPOME Treatment

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A R T I C L E   I N F O

A B S T R A C T

This study basically compared the adsorptive efficacies of powdered activated carbons (PACs) produced from palm empty fruit bunches (EFB) in the treatment of a non-simulated biotreated palm oil mill effluent (BPOME). Each of the PACs was produced from two different methods namely steam- and CO₂-activation routes. This test was performed with the main aim of obtaining an appropriate activated carbon suitable for the treatment of BPOME. The steam activated PAC was found to possess higher adsorptive strength as compared with that of CO₂ activation with the operating conditions of 150 rpm agitation for 60 min with varying dosage of PAC from 0.5 – 5.0 g. The steam activated PAC performed better than the CO₂ activated PAC with a record uptake of up to 81%, 92% and 89% for Chemical Oxygen Demand (COD), Manganese (Mn) and Hydrogen Sulfide (H₂S) respectively as compared with the uptake of 67%, 90% and 87% from the CO₂-activated PAC. Furthermore, a 2-level full factorial design of experiment was utilized to assess the effects of three factors on adsorption. The highest removal efficiencies for COD, Mn and H₂S were found to be 83.1%, 93.6% and 89.8% at adsorbent dosage 5 g, agitation speed 200 rpm and contact time 60 min.

INTRODUCTION

Accessibility to clean water is currently shrinking, thereby putting man under severe threat of water borne diseases. Besides the increasing world population, which is directly proportional to water demand, the volume of fresh water available for domestic use is also being tapped for use by industries and consequently the used water are being injected as discharge into the fresh water bodies thereby rendering them unsafe for use [1-4]. We are however fortunate to be existing in a world whereby the awareness of the detrimental effects of these pollutions are on the increase as this awareness shall help in ensuring the protection of our biosphere, conserving our conventional natural resources and safeguarding the future generations [5, 6].

Though water seems not to be a problem of Malaysia, however, Department of Environment (DOE) reported that the Country's clean river basins decreased from 55% to 50% from year 2006 to 2010 due to the increase in pollution trend [7]. The Department further observed that the decrease in the number of clean rivers were attributed to an increase in the number of polluting sources such as agro-based industries [7].

One of the major players of the agro-based industries is the palm oil industry. It is estimated that before 1 ton of crude palm oil (CPO) can be produced from the palm fruit bunches, 5 – 7.5 tons of water are usually utilized and more than 50% of this water usually end up as POME and eventually discharged into the rivers after some low level treatments [8]. The treatments are basically anaerobic and aerobic, which are incapable of rendering the treated wastewater reusable [7,9]. In the year 2012 alone, 55.22 million tons of POME was generated (http://www.ggs.my/index.php/palm-biomass). This indicates that in the year 2012, the production of 18,785,030 tons of CPO must have utilized at least 93,925,150 tons of fresh water.

From the foregoing, there is the need to polish the discharge for in-house processes reuse in the industry in order to conserve the fresh water sources. Various treatment methods have been proposed for this purposes, however adsorption process involving the use of activated carbon has attracted interest due to its efficacy, availability and cost-effectiveness. Various activation processes have been reported for PAC production from

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EFB ranging from physical such as steam and CO_2, to chemical activation [10-14]. Moreover, these researches have assessed the dissolved organics and inorganics removal potential of EFB-PAC in only the simulated or synthetic wastewater media which calls for further assessment of ideal adsorbed solutions (IAS) so as to establish experimental facts that can stand scrutiny in the realistic process designs.

This work is interested in employing the physically activated PACs because it brings about cheaper production as compared with the chemical activation [15]. The objective of the present work is to explore the potential of using EFB-PAC, locally prepared by physical activation, as a low cost adsorbent for the reduction of COD, Manganese and Hydrogen Sulfide from BPOME, which is an ideal adsorbed solution (IAS), as it is believed that only such media could reveal the true potential of the adsorbent. The results of the removal of these constituents will depict the adsorbents' strength in the removal of dissolved organics, inorganics and gases from BPOME.

MATERIALS AND METHODS

Activated Carbon Pre-Cursor (EFB) and Biotreated Palm Oil Mill Effluent (BPOME) Sampling:

Samples of empty fruit bunches (EFB) to be utilized as pre-cursor for the PAC production, as well as the BPOME samples (wastewater) were collected from Sime Darby Palm Oil Mill in Carey Island, Malaysia. The EFB was preserved in a cooling room at 4 °C. The EFB was later washed, dried at 105 °C for 24 hours in oven for dehydration until constant weight was achieved and crushed to desired particle size before the carbonization and activation treatments were performed.

Production of Activated Carbon:

The optimized operating conditions of 900 °C activation temperature, CO_2 gas flow rate of 0.1 L/min and activation time of 15 min. for the CO_2 activation reported elsewhere [13] were strictly adapted. The PAC was characterized to have a BET surface area of 345.1 m²/g. On the other hand, the optimum operating conditions of 900 °C activation temperature, steam flow rate of 2.0 mL/min and activation time of 15 min. for the steam pyrolysis activation treatment resulting in 635.16 m²/g BET surface area reported elsewhere [10] were adapted.

Adsorption Tests:

The preliminary batch adsorption experiments were carried out on BPOME sample to evaluate the adsorption prowess under varying PAC dosage of 0.5 - 5.0 grams (in 100 mL of solution) at 150 rpm agitation for 60 minutes. This was done to specifically identify the better PAC among the steam- and CO_2-activated types in the uptake of COD, Mn and H_2S, at the fixed conditions mentioned above.

Further adsorption tests were carried out using a 2-level (2^3) full factorial design (FFD) with three center points for the optimization of adsorption process (Table 1.). The data ranges were selected based on the preliminary results coupled with previous works. The total number of experiments for the adsorption optimization as unveiled by the design of experiment statistical software using *Design-Expert®* Version 7.0.0 was 11. Analyses of the wastewater before and after treatment water were carried out following the Standard Methods for the Examination of Water and Wastewater [16].

**Table 1:** Experimental factors and their levels for full factorial design (FFD)

Factor	Name	Actual (low)	Actual (high)
A	Dosage, *g*	2	5
B	Agitation, *rpm*	100	200
C	Contact Time, *min.*	30	60

RESULTS AND DISCUSSION

PAC Characterization:

Few characterization analyses were performed on the PAC produced just to confirm if the PACs have been successfully re-produced from the adapted methods. The resulting PACs from the two treatments were found to have approximately the same moisture content of 6%, bulk density of 1 g/cm³, ash content of 8%, and average yield of 25%. These values conform with the previously established ones [10, 13]. However, the specific surface area using the methylene blue (MB) method by spectrophotometry was found to be 1185.3 m²/g for the steam-activated PAC and 712.48 m²/g. These discrepancies when compared with the previous works were expected as they were determined using BET nitrogen method. In normal circumstances, the specific surface areas determined by low-temperature nitrogen adsorption isotherms (BET method) usually exhibit moderately low values when compared with MB methods due to the fact the BET method only measures in terms of "external surfaces" while the MB measures in terms of the "total specific surfaces" [17-20]. Fig. 1 (a & b) represent the SEM images showing the opened pores in the PACs. It could be observed that combinations many large and fine pore are contained in Fig. 1 (a) which represents the steam-activated PAC. The developed pores are near-uniform.

However, the pores formed in Fig. 1 (b) for the CO_2-activated PAC are non near-uniform as there are very few large pores with a few fine pores.
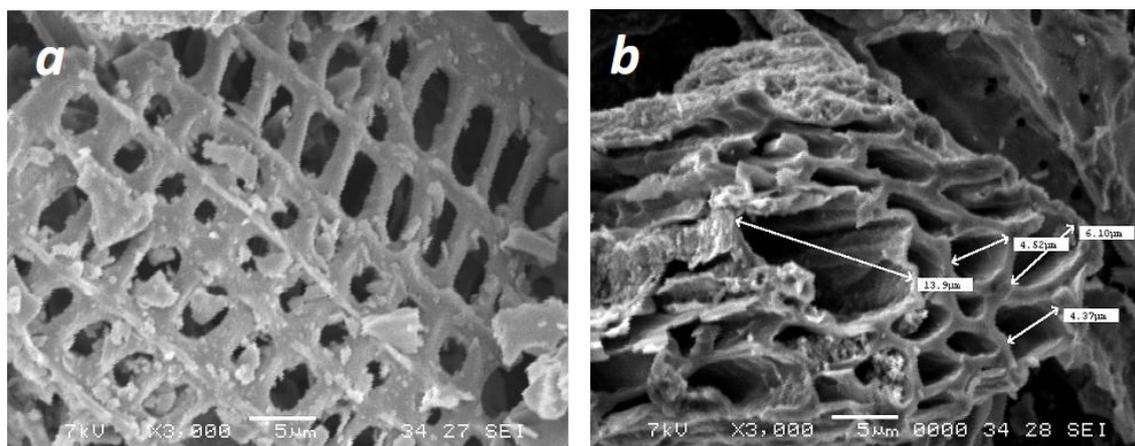

Fig. 1: SEM microphotographs of: *a* – Steam activated PAC; and *b* – CO_2 activated PAC

Adsorption Experiments:

        Table 2 shows some of the various constituents present in BPOME as received from industry together with their levels after 24 hours of sedimentation process. Figs. 2, 3 and 4 depict the percentage removal of COD, Mn and H_2S respectively. In Fig. 2, the steam-activated and CO_2-activated PACs exhibited 81% and 67% COD uptake efficiency, with the residual contents of 270 mg/l and 455 mg/l, respectively. It was also observed that adsorption on both PACs started tending towards their equilibrium states, with different uptake efficiencies, at over an adsorbent dosage of 3 grams/100 mL. Similar conclusions on adsorbent dosage and removal efficiency plots have been drawn by Ahmedna *et al.,* [21] and Devi *et al.,* [22].

Table 2: Level of Contaminants in BPOME

Contaminants	As-Collected Values	After Sedimentation
Turbidity (NTU)	1050	840
TDS (mg/L)	1207	970
COD (mg/L)	1730	1387
Fe (mg/L)	ND	ND
Mn (mg/L)	3.08	2.14
H_2S (mg/L)	0.88	0.6
Ca Hardness (mg/L)	240	200
Mg Hardness (mg/L)	1800	1480
Silica (mg/L)	73	58
P. Alkalinity (mg/L)	180	160
T/M Alkalinity (mg/L)	2000	1700
SS (mg/L)	761	284
pH	8.65	8.56
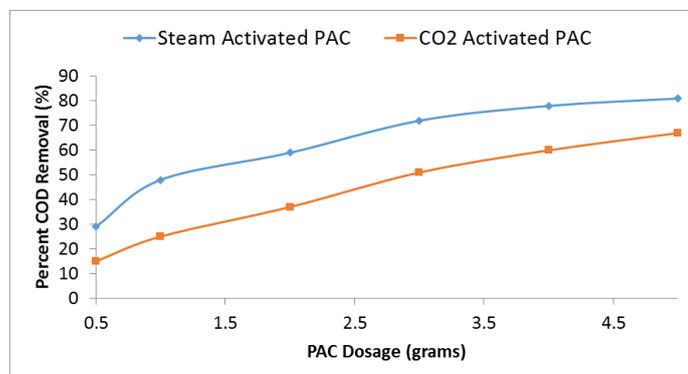
Fig. 2: Comparative Adsorption Efficiencies of Steam & CO_2-activated PAC with respect to COD removal
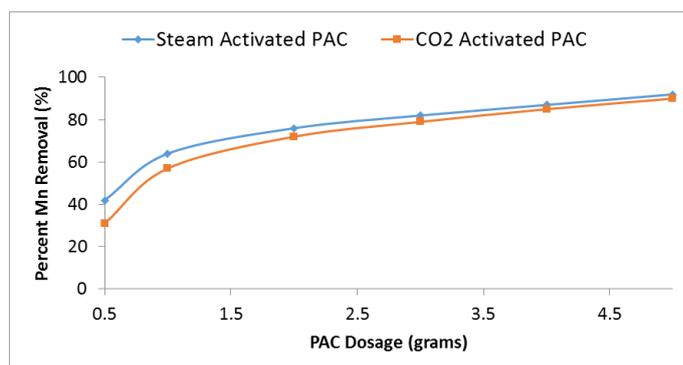
Fig. 3: Comparative Adsorption Efficiencies of Steam & CO_2 activated PAC with respect to Manganese (Mn) removal
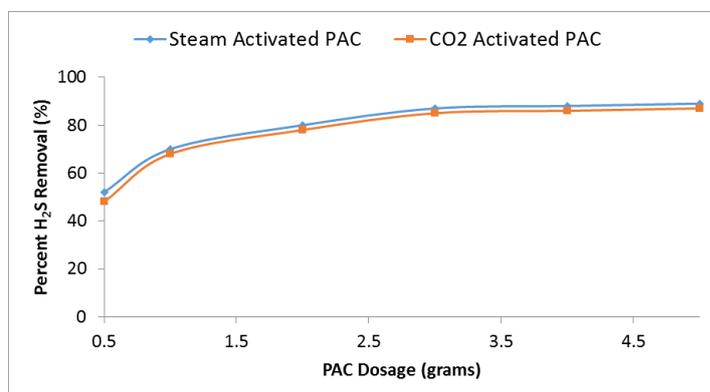
Fig. 4: Comparative Adsorption Efficiencies of Steam & CO_2 activated PAC with respect to Hydrogen Sulfide (H_2S) removal

The same trend was observed in the case of the Manganese uptake as the adsorption process tends towards equilibrium at the same dosage of 3 grams. Furthermore, the uptake efficiency was also relatively better with the steam-activated PAC when it exhibited 92% Mn removal as against the CO_2-activated PAC exhibited 90% removal leading residual contents of 0.178 mg/L and 0.21 mg/L of Mn, respectively. Very close uptake efficiencies were observed between the two activated carbon types in the case of H_2S uptake from inception of the experiment. The steam-activated PAC attained 88.8% uptake while that of CO_2-activated PAC achieved 86.8% uptake efficiency with the residual contents of 0.067 mg/L and 0.079 mg/L, respectively. Closeness in the performance efficiencies in Mn and H_2S uptakes could be attributed to the nature of the pore structures formed in the two PACs which is the presence of some fine pore structures, ideal for the adsorption of low molecular size compounds from either liquid or gaseous phase. These fine- or micro-pore structures are usually arrived at through the steam-activation process of PAC production [23]. It is crystal clear that steam-activated PAC performed better than the CO_2-activated in the COD uptake with relatively wide gap. COD is an organic contaminant with relatively bigger size as may be compared with Mn and H_2S, and physically the best activated carbon adsorption usually occurs when pores are barely large enough to admit a contaminant molecule especially the relatively larger molecules which is an indication of the presence of larger pores capable of adsorbing larger molecules. Nonetheless, the filter surface of the PAC may have also interacted chemically with the organic molecules. As a rule of thumb, large organic molecules are most proficiently adsorbed by activated carbons, and similar materials tend to associate. Since organic molecules and activated carbon are similar materials, there is a stronger tendency for most of the organic compounds to associate with the activated carbon thereby leading to better adsorption performance [24]. Usually the least soluble organic molecules are most strongly adsorbed. Also, the smaller organic molecules are often held the tightest due to the fact that they fit into the smaller pores of the activated carbon. From the preceding, the presence of the combination of both fine and larger pore structures, and possible chemical interactions may be responsible for the steam-activated PAC's better performance than the CO_2-activated PAC which may also be attributed to the existence of relatively lots of fine pores but restricted larger pore structures not capable enough for larger organic molecule uptake [23-27].

Many of the works available on the uptake efficiency tests of EFB-based PAC are based on simulated

environment and up to or above 90 % of the dissolved constituents could be removed [10-13]. Single component adsorptions like these usually exhibit such performances unlike complex or multicomponent adsorptions. In most practical adsorption processes usually termed as IAS, there are usually more than one component to be adsorbed from either an aqueous or gaseous media. Therefore, adsorption capacity measurements of the multi-component mixtures are much more complex than for a single adsorbate [28-30]. Correspondingly, interactive and adsorptive competitions are expected among the several adsorbates present in BPOME (Table 2) until all the available pores are blocked by them. Therefore, the relatively low adsorption strength of the adsorbents may be due to the aforementioned facts.

Statistical Optimization of the selected PAC adsorption strength Using 2-level (2^3) full factorial design (FFD):
     A 2-level full factorial design was used for the adsorption experiments of the selected steam-activated PAC in order to obtain the relation between the variables affecting the performance. Adsorbent dosage, contact time and agitation speed were factors employed for the experimental design (Tables 1 and 3) for the removal of COD, Mn and H_2S. From the 11 experimental runs, the results were analyzed using the analyses of variance (ANOVA). ANOVA is a statistical algorithm that subdivides the total variation in a set of data into element items relating to specific sources of variation for the purpose of testing hypotheses on the parameters of the model [31]. The statistical significance of the ratio of mean square variation due to regression and mean square residual errors were tested using the ANOVA technique.

Table 3: Experimental Design (2^3) for the determination of Optimum Operating Conditions for Adsorption Process

RUN	A: Dosage, *g*	B: Agitation, *rpm*	C: Time, *mins*	COD, *mg/L*	*%R* for COD	Mn, *mg/L*	*%R* for Mn	H_2S, *mg/L*	*%R* for H_2S
1	2	200	30	249	82.0	0.156	92.7	0.073	87.8
2	3.5	150	45	242	82.6	0.142	93.4	0.062	89.7
3	5	100	60	246	82.3	0.146	93.2	0.066	89.0
4	5	100	30	250	81.9	0.142	93.4	0.072	88.0
5	2	200	60	249	82.0	0.157	92.7	0.067	88.8
6	3.5	150	45	240	82.7	0.143	93.3	0.063	89.5
7	5	200	30	237	82.9	0.138	93.6	0.067	88.8
8	5	200	60	235	83.1	0.138	93.6	0.061	89.8
9	2	100	30	254	81.7	0.164	92.3	0.084	86.0
10	2	100	60	252	81.8	0.166	92.2	0.076	87.3
11	3.5	150	45	240	82.7	0.143	93.3	0.063	89.5

     The highest removal efficiencies for COD and H_2S were respectively found to be 83.1% and 89.8% at adsorbent dosage 5 g, agitation speed 200 rpm and contact time 60 min. That of Mn was found to be 93.6% at two operating conditions of adsorbent dosage 5 g, agitation speed 200 rpm and contact time 60 min., and adsorbent dosage 5 g, agitation speed 200 rpm and contact time 30 min. It was also experiential that the optimized parameters are almost close to each other in the experimental runs and that some factors exhibited significant effects ($p < 0.05$) while non-significance ($p > 0.05$) effects were attributed to others.
     To explain further, the Model F-values of 35.79, 6.366E+007 and 152.36 in the ANOVAs for COD, Mn and H_2S adsorptions imply the models are significant. There are only 2.74%, 0.01% and 0.65% chance that "Model F-Value" these large in each case could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant.
     In the case of COD uptake, factors A, B, AB are significant model terms with an R^2 of 0.9921. Values greater than 0.1000 indicate the model terms are not significant. The "Curvature F-value" of 55.68 implies there is significant curvature (as measured by difference between the average of the center points and the average of the factorial points) in the design space. There is only a 1.75% chance that a "Curvature F-value" this large could occur due to noise. Also, "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Here, the ratio of 18.191 indicates an adequate signal. This model can be used to navigate the design space. The final regression equation in terms of actual factors is given in (1):

$$COD\ Residual = +512.67 + 4.67A + 0.01B - 0.056C - 0.06AB$$
$$- 0.056AC + 4.44E - 004BC + 1.11E - 004ABC \tag{1}$$

     ANOVA for the Mn uptake revealed that only the factors A and B are significant model terms with an R^2 of 1.00. Values greater than 0.1000 indicate the model terms are not significant. The "Curvature F-value" of 6.366E+007 implies there is significant curvature (as measured by difference between the average of the center points and the average of the factorial points) in the design space. There is only a 0.01% chance that a "Curvature F-value" this large could occur due to noise. Since the standard deviation is 0.00, there was no measurement for Adeq Precision. This model can be used to navigate the design space. Here, the final regression equation in terms of actual factors for Mn residual is as given in (2)

$$\text{Mn Residual} = +0.374 - 0.019A - 2.10E\text{-}004B + 1.33E\text{-}004C + 4.00E\text{-}005AB \qquad (2)$$
$$+ 6.67E\text{-}005AC - 1.11E\text{-}007BC - 4.44E\text{-}007ABC$$

Lastly for regarding the ANOVA for H_2S uptake by adsorption, it was observed that factors A, B, C, and BC are significant model terms with an R^2 of 0.9981. Values greater than 0.1000 indicate the model terms are not significant. The "Curvature F-value" of 427.68 implies there is significant curvature (as measured by difference between the average of the center points and the average of the factorial points) in the design space. There is only a 0.23% chance that a "Curvature F-value" this large could occur due to noise. Also, "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Here, the ratio of 44.042 indicates an adequate signal. It is also certified that this model can be used to navigate the design space. For this, the final regression equation is given is given in (3) below:

$$H_2S \text{ Residual} = +0.043 + 1.00E\text{-}003A + 1.03E\text{-}004B + 6.00E\text{-}004C + 3.33E\text{-}006AB$$
$$\qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \dots\dots (3)$$
$$+ 3.33E\text{-}005AC - 3.11E\text{-}006BC - 1.11E\text{-}007ABC$$
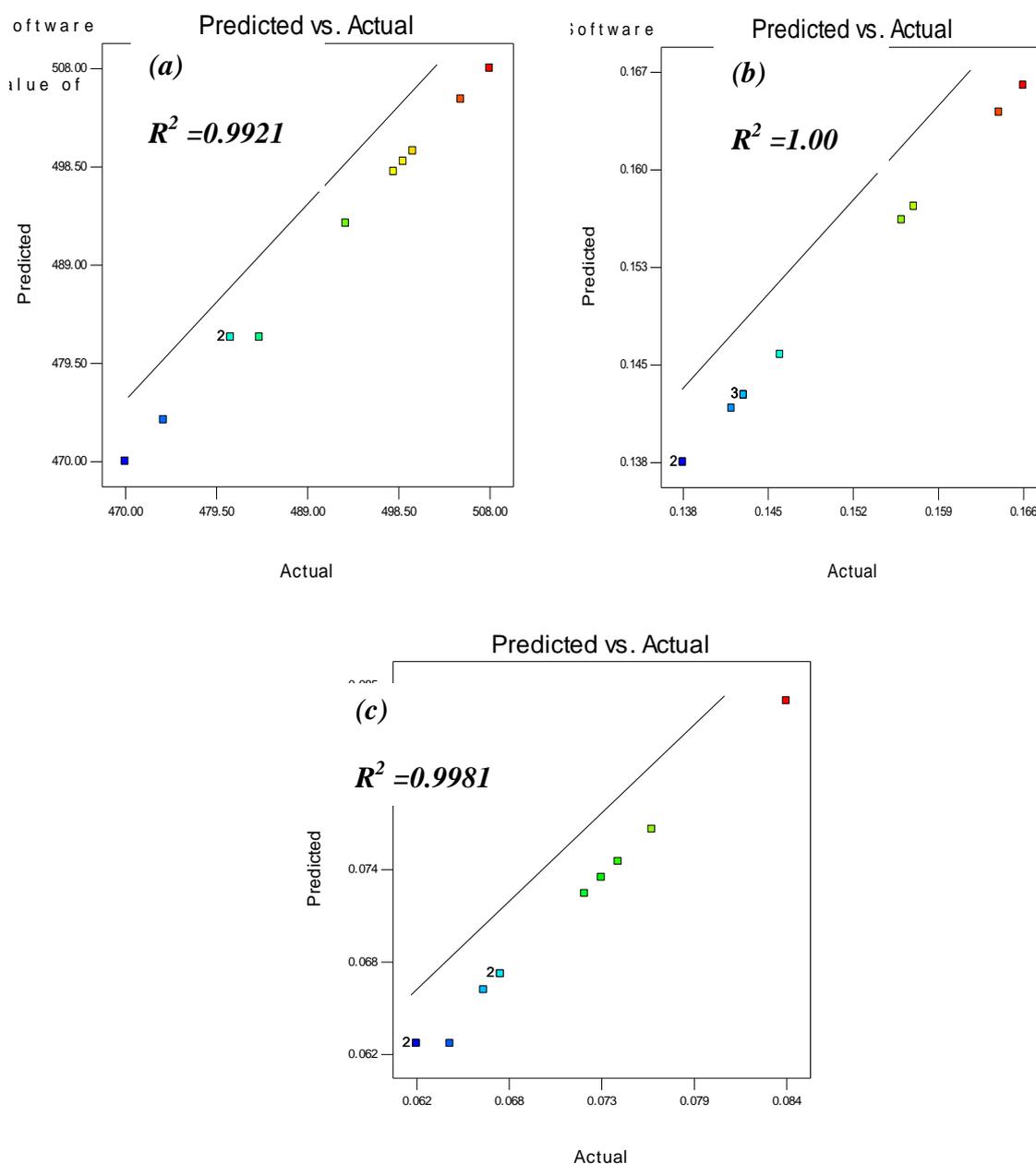
Fig. 5: The predicted vs. actual plot depicting the (a) – COD, (b) – Mn, and (c) - H_2S residual values.

   Figs. 5 (*a,b &c*) depict the predicted versus the actual values for COD, Mn and H_2S uptake by the activated carbon respectively. It is crystal clear that the predicted values obtained were pretty close to the actual values which is indicating that the models developed were efficacious in spanning the correlation between the factors and respective uptakes. The qualities of the developed model were evaluated based on the coefficient of determination values. Experimental values of the three responses were correlated with the predicted responses as could be observed from the Figures above. The coefficients of determination R^2 of 0.9921, 1.00 and 0.9981 indicated that 99.2%, 100% and 99.8% of the variations in COD, Mn and H_2S uptakes could be respectively elucidated by the independent variables: adsorbent dosage, agitation speed and contact time. All the three R^2 values obtained were very high indicates that there were good agreements between the predicted and actual values from the models. These are adequate approximations of the true response function. Besides, it was also observed that R^2 values are in reasonable agreements with the respective adjusted R^2 values of 0.9644, 1.00 and 0.9916 respectively for COD, Mn and H_2S uptakes. The models equations exhibited the standard deviations of 1.15, 0.00 and 5.774E-004 for Eqs. (1), (2) and (3), respectively. The closer the R^2 value to unity and the smaller the standard deviation, the better the model and this gives a buoyancy of established closeness between the actual and predicted values for the responses.
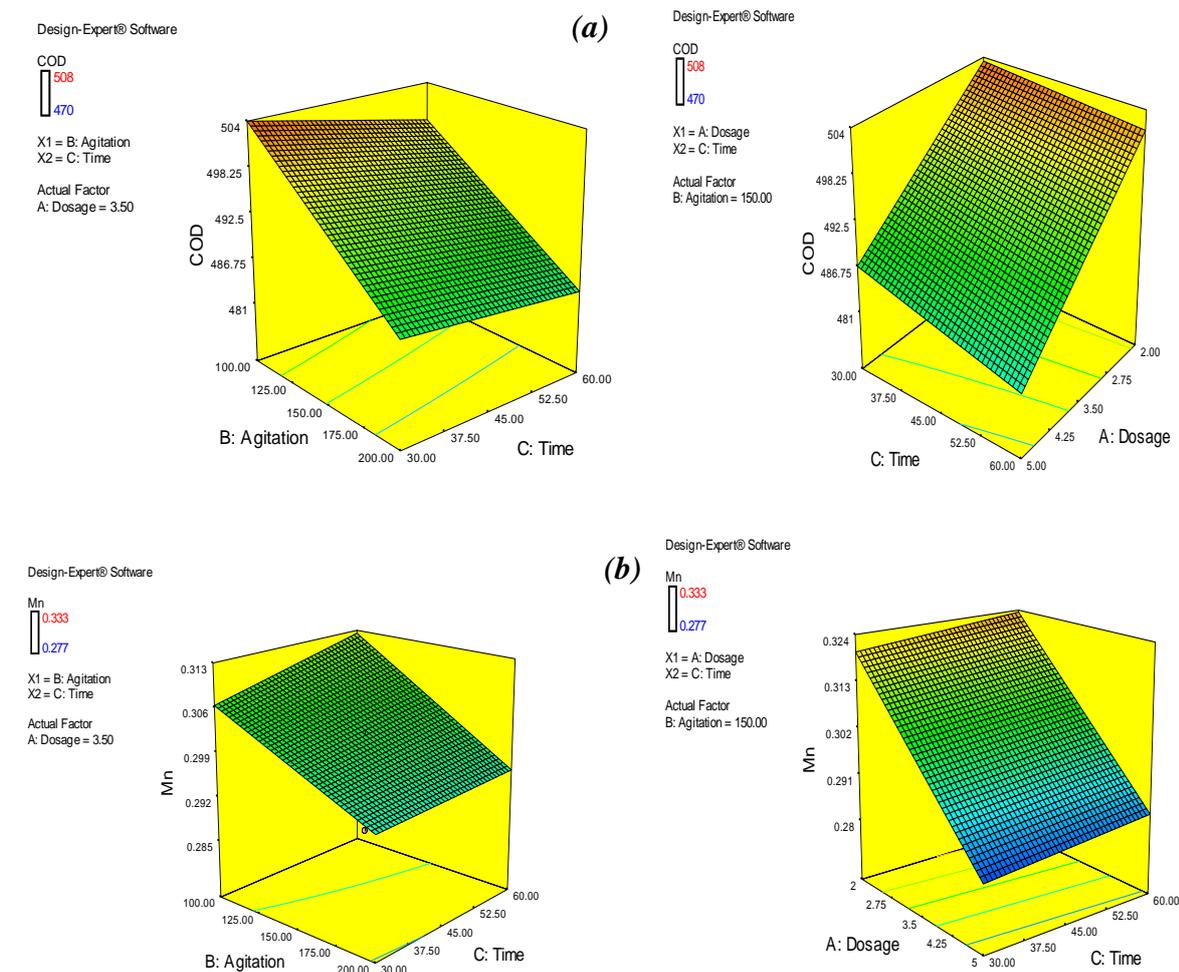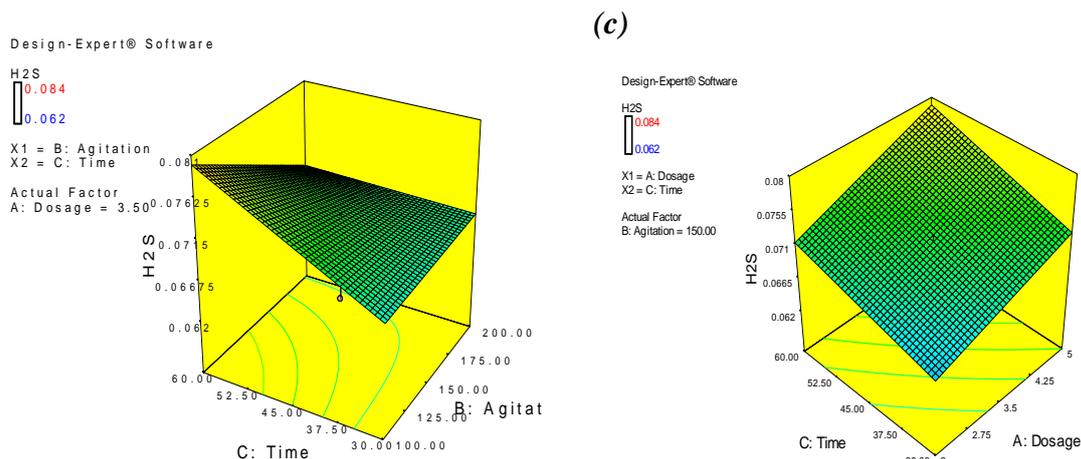
Fig. 6: 3D surface plots showing the effects of operating factors on the adsorption performance in terms of (a) COD uptake, (b) Mn uptake, and (c) H_2S uptake of the steam-activated PAC.

In design of experiments, the 3D and 2D graphical representations of model equations facilitate examinations of the effects of operation parameters. Fig. 6 shows some of the 3D surface plots revealing the interactions between the adsorption operating factors/conditions. These results illustrate the ripostes of the three factors that are involved in the experimentation. Fig. 6 (a) shows the relationship between the agitation speed and contact time. The increase in the agitation between 100 – 200 rpm as well as time between 30 – 60 min resulted in the increase in COD uptake which lowers its residual concentration. Still on COD uptake, the adsorbent dosage and contact time relationship was analyzed and it was evident from the 3D plot that there were generally an increase in COD uptake as the dosage and contact time were increased between 2 – 5 g and 30 – 60 min respectively. It is pertinent to note that the contact time is not as significant in COD uptake as do the agitation speed and adsorbent dosage. This is evident from the very slight disparities exhibited by the contact time axes in the two 3D plots presented in Fig. 6 (a).

Same trend was observed for the Mn uptake as the interactions among the factors (Fig. 6 (b)) were similar to that recorded for COD. Here also, there are very significant effects exhibited by the agitation speed and adsorbent dosage but relatively lower significant effect was observed for contact time.

As for H_2S uptake, it could be observed the 3D plot (Fig. 6 (c)) representing the interaction between contact time and agitation speed shows some sort of curvature which is an indication of a good interaction between the two factors. The results show that the agitation speed and contact time have significant effects in H_2S uptake.

The statistical analysis of the *Design-Expert*® Version 7.0.0 software thereby offered 18 numerical solutions of optimum conditions with the desirability values ranging from 0.818 – 1.000 for the highest uptake of the three pollutants from BPOME. The validation was done on the basis of selected optimum factors as numerically determined for best COD, Mn and H_2S uptakes with a high desirability of 1.000 were adsorbent dosage of 5 g, agitation speed of 200 rpm and contact time of 60 min.

Conclusion:

This study has successfully evaluated the buoyancy of EFB-PAC produced through the steam and CO_2 activation methods in the uptake of organic (COD), metal (Mn) and gas (H_2S). Comparison of the performances of both steam- and CO_2-activated PAC in the real wastewater (BPOME) treatment revealed the steam-activated PAC to be of better performance in the uptake of dissolved organic (COD), metal (Mn) and gas (H_2S). Further optimization study of the operating conditions was done using the full factorial design and ANOVA analyses, especially the coefficients of determination R^2 values, revealed the interactions between the factors involved in the adsorption experiments viz. the agitation speed, adsorbent dosage and contact time. The software further gave the optimum factors for the best uptake of the three pollutants and adsorbent dosage of 5 g, agitation speed of 200 rpm and contact time of 60 min was selected and validated.

Additionally, the application of this low cost adsorbent utilizing the industrial solid waste (such as EFB) in the treatment of the industrial wastewater could be a better way of zero waste practice.

Furthermore, the results from this study have confirmed the suitability of the locally produced PAC to be applied in primary treatment steps prior to any other secondary/tertiary treatments in the reclamation and reuse programs, such as industrial boiler-feed and/or process utilities [8], when handling wastewaters having constituents closely related or less than what are contained in BPOME.

ACKNOWLEDGEMENTS

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