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Efficiency of food waste activated carbon in treating biodiesel plant effluent: Impact on process conditions and NaOH recovery

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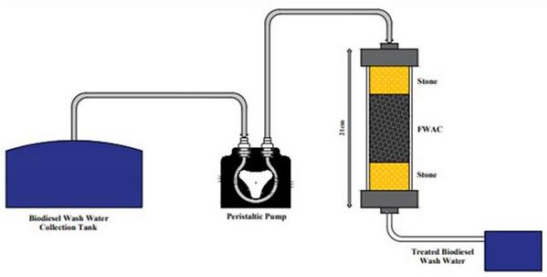
Graphical abstract



Abstract

The technologies which provide alternate to conventional fuel has led to the production of biodiesel. The source of biodiesel wash water generation takes place during the production of biodiesel via transesterification process. Biodiesel wash water is one of the significant side streams generated during biodiesel production from waste cooking oil. Thus, the generated biodiesel wash water has high pH, turbidity, methanol, soap and glycerol. In the present study, a solution to treat and to bring down the concentration of each of the contaminants have been studied by using zinc chloride activated carbon derived from the food waste. The mixed food waste reject was carbonized and further activated with zinc chloride for biodiesel wash water treatment experiments. The food waste activated carbon (FWAC) and commercial activated carbon (CAC) were analyzed for structural and surface morphology using X-ray diffraction (XRD), Filed emission scanning microscopy (FE-SEM) and IR-Raman spectroscopy. The adsorption experiments were performed at 10 to 50 minutes with an adsorbent dosage of 0.1 to 0.5 in 100 mL of biodiesel wash water. pH, turbidity and total dissolved solid (TDS) of biodiesel plant effluent before and after adsorption experiments were determined. Food waste-activated carbon used for the study reduced the effluent pH from 11.5 to 7, Turbidity from 435 NTU to 1 NTU and TDS from 1140 mg/L to 145 mg/L. The feasibility of NaOH recovery from biodiesel wash water was also studied.

Keywords: Biodiesel wash water, activated carbon, adsorption, TDS, sodium hydroxide

1. Introduction

The modernized world is attributed to various concerns like treating industrial effluents, freshwater shortage and strategies for tackling environmental pollution. The increasing demand has not only resulted in the depletion of non-renewable fossil fuels but has also contributed to higher carbon emissions. Hence, it is necessary to find renewable sources for green fuel generation with lesser environmental concerns (Aman *et al.* 2023). The development of biodiesel industries based on second-generation raw materials has been enormous in the last decade. However, higher productivity paved the way for generating a large quantum of washwater that needs to be treated before its disposal into waterbodies (Daud *et al.* 2015) (Al-Basir *et al.* 2019). Transesterification of triglycerides catalyzed by alkali is a well-established process for biodiesel production (Atadashi *et al.* 2011; Min *et al.* 2023; Radjarejesri *et al.* 2023). Like production units, including paper and pulp, the food industry, textiles, pharmaceuticals and plastics, biodiesel production also consumes enormous amounts of water.

Washing is a significant step that defines biodiesel quality (Diaz *et al.* 2020). The number of washing cycles is determined by oil quality, the process conditions, etc. (Kilicarslan *et al.* 2023). Every batch of washing generates approximately five times the quantity of biodiesel (Bashir *et al.* 2018). The discharged biodiesel washwater is alkaline, turbid, and contaminated with unreacted esters and acids, making it unsuitable for disposal onto the land and water, affecting the metabolic activities of the organisms dwelling in that environment. These, in turn, have endangered humanity's long-term survival. Owing to these terms, finding new regimes for sustainable wastewater treatment and management is necessary. Biodiesel washing process produces huge amount of washwater effluent. An author has tried treating the washwater with the nanofiltration process for depicting the potential of washwater reuse (K. Mozaffarikhah *et al.*2017).

Bioconversion and thermochemical conversion are reported as clean food waste recycling techniques (Xiong

et al. 2019; Suhartini *et al.* 2022). Due to its high carbon content, food waste is pyrolyzed to synthesis carbonaceous materials, which are activated further by chemical or physical methods to increase porosity (Grycova *et al.* 2016). Phosphoric acid, Hydroxides and Carbonates of potassium or sodium, Chlorides of Aluminum, Zinc or Magnesium are usually used biomass activating agents, activated at 450–900 °C to produce activated carbon (Nanda *et al.* 2016).

Several waste derived activated carbon have been synthesized and attempted for treating alkaline waters (Hemamathi *et al.*2023). Biodiesel wash water is highly alkaline. The wash water generated during the conversion of waste cooking oil to biodiesel reported earlier (Ranjan *et al.* 2022). Taken up for this study. The waste cooking oil biodiesel has been established in the Sathyabama Institute of Science and Technology campus has a waste to energy conversion incitive with the increasing number of inmates in the institution the food waste generated is also increasing (Priyadharsini *et al*. 2021). Several methodologies have been investigated for effective utilization of food waste. The heterogeneity of food waste makes it a challenging source for other identified applications, where the carbohydrate content needs to be isolated. However mixed food waste has been effectively converted into $ZnCl_2$ activated carbon in the pervious study (Santhosh and Dawn 2021). To treat the was water using 900 Kg of food indigenously was the objective with which this study has been done. So as to develop a process promoting circular economic. By diverting 25% of the food waste generated for activated carbon synthesis.

For the adsorption studies, food waste-based activated carbon was synthesized with 2N zinc chloride solution and used to treat biodiesel washwater. The adsorption experiments at varying times (0 to 50 min) and adsorbent dosage (0.1 to 0.5 g) were performed in a customized adsorption column with synthesized activated carbon as bed material. The pH, TDS and turbidity of the washwater before and after adsorption experiments were noted. Further titration experiments were performed to depict the efficiency of NaOH recovery from the washwater.

2. Materials and methods

2.1. Food waste activated carbon (FWAC) synthesis

Food waste was collected from Sathyabama Institute of Science and Technology Chennai, Tamil Nadu, India. The sources for the food waste collection are the boy's hostel mess, the girl's hostel mess and the dental college mess in the institution. Proximate analysis of the collected food waste was done as per ASTM D1762-84. Food waste was sundried and oven-dried subsequently for 6 hours. The temperature was maintained at 105°C. Food waste was incinerated at 350°C for 150 minutes and heated in a muffle furnace.

The food waste activated carbon was milled for 20 minutes to reach 50 mesh size. The obtained carbon powder was activated using 95% pure zinc chloride purchased from Fisher Scientific Mumbai. The synthesized carbon powder was doped in 0.5 N to 3.5 N solution with varying conditions of temperature (80°C) and time (90 mins) was used. Further activation of the $ZnCl_2$ doped carbon samples was done for 120 minutes in a muffle furnace set at 600°C (Santhosh and Dawn 2021**).** The activated samples were size-reduced and then washed with distilled water until the pH reached neutral. The food waste activated carbon obtained was oven-dried for 2 hours at 110°C.

2.2. Food waste activated carbon characterization

The properties of $ZnCl_2$-activated food waste-based carbon samples before (FWAC) and after adsorption (WTFAC) were compared with commercial activated carbon before (CAC) and after adsorption (TCAC). The crystalline or amorphous nature, surface morphology and presence of functional groups were analyzed using X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM) and Fourier transform-infrared spectroscopy.

2.2.1. Raman shift

This study used a Raman confocal microscope (In Via Reflex, Renishaw, UK) to analyze the food waste-activated carbon with the excitation source at 532 nm (green laser) and a grating of 2400 lines/mm. For the measurements, a 50X objective was employed with the spectral range 100 – 3000 cm^{-1} spectral resolution of ~0.5 cm^{-1}, providing a diffraction-limited spot on the sample. Instrumental correction was made with the standard silicon characteristic band at 520.5 cm^{-1}. Renishaw's Wire 5.2 software was used to determine the band position. The spectra were further smoothed to remove signal noise and to confirm the accurate band position. Origin Pro 8 software was used to obtain the data for further information.

2.2.2. XRD characterization

The XRD analysis was the most preferred technique to examine the crystalline and non-crystalline nature of the material. Phase analysis and the nature of activated carbon were confirmed by performing X-ray diffraction studies. D/Max-2500 X-ray diffractometer equipped with Cu-Kα radiation (1.5406 Å) operating at 40 kV, 50 mA in the 2θ range of 20°–80° with a scanning rate of 0.02 S1 was used for the study.

2.2.3. FESEM

The FESEM analysis of prepared activated carbon was done using a Scanning Electron Microscope (FESEM)-SUPRA 55-Carl Zesiss, Germany.

2.3. Biodiesel wash water

This study used a large quantity of waste cooking oil generated in the Sathyabama Institute of Science and Technology canteen mess to produce biodiesel as an initiative towards responsible consumption and production (SDG-12), clean water and energy (SDG-6 & 7). Detailed experimental studies on biodiesel production from waste cooking oil and its results were reported in the previous study (Santhosh and Dawn 2021**)**. Precisely the operating conditions like methanol/oil molar ratio (6:1), alkaline catalyst (5 g), reaction time (90 min) and reaction temperature (60°C) were studied. It was found that the maximum biodiesel conversion efficiency was 96%. The

physical and chemical properties of biodiesel were found to be in the requirement of relevant international standards (ASTM D6751). Produced biodiesel was tested for the operating agriculture pump sets, gensets and diesel engines.

In biodiesel production, washing is inevitable, generating an enormous amount of biodiesel wash water. The washing process was repeated till the pH level of the wash water reached neutral. In a pilot scale of 40 L capacity, wash water of around 110 L will be generated. The generated wash water has a pH of 11.5, TDS of 1040 mg/L and Turbidity of 450 NTU, respectively. For comparison, wash water collected by washing of biodiesel obtained from various sources has been investigated and the properties of wash water are compared as shown in Table

Name of the oil and biodiesel wash water	pH	TDS (mg/L)	Turbidity (NTU)
Waste cooking oil biodiesel wash water	11.5	1040	435
Groundnut oil biodiesel wash water	9.3	88	180
Rice bran oil biodiesel wash water	9	96	200
Grape seed oil biodiesel wash water	9.5	95	216
Beef tallow biodiesel wash water	10.3	96	162
Pongamia oil biodiesel wash water	10.5	89	508

2.4. Adsorption studies

Adsorption studies on biodiesel wash water were performed with fixed bed adsorption column studies with varying times (10 to 50 min) and activated carbon dosage (0.1g to 0.5 g). The schematic diagram of the fixed bed column with the adsorbent bed as FWAC and CAC, silica bed, collection tank, and peristaltic pump is shown in Figure 1. The column used in the study had a height of 21 cm and an internal diameter of 5.5 cm. Carbon material was loaded to 10 cm (i.e. 22.85 g), and the top and bottom of the carbon material were loaded with silica stone (5 mm diameter approx) of approximately 5 cm. A sponge of 1.5 mm was placed on the column's top and bottom surface individually between the carbon and silica stones. A silicon pipe of 0.8 cm diameter was connected with flange joints at the bottom of the column to provide an inlet. The wash water's properties like pH, TDS, and Turbidity were studied.

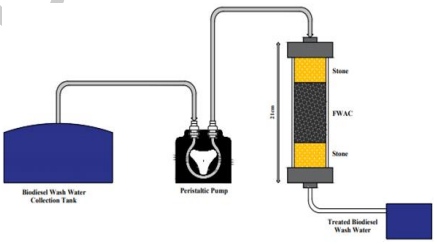


Figure 1. Schematic diagram of fixed bed column

2.5. NaOH estimation in washwater and adsorbed washwater

The excess amount of sodium hydroxide in the washwater was estimated to predict the feasibility of recovering it for further studies. A titration experiment was performed to initiate the precipitation of NaOH from the washwater. About 20 mL of treated washwater was taken in a conical flask and 1 N HCl solution was taken in the burette. Upon titration of both washwater and HCl, the experiments were stopped once a pale pink solution was seen in the conical flask. The amount of burette solution (1 N HCl) was noted and substituted in the below formula to estimate the amount of NaOH present in the solution.

$$V_1N_1 = V_2N_2$$

V_1 is the volume of washwater taken (20 mL), V_2 is the volume of 1N HCl consumed in the titration process, N_1 is the unknown concentration of NaOH present in the washwater and N_2 is the Concentration of HCl solution. The pale pink solution precipitates in the next 2-3 min. If not, a small quantity of methanol was added to the titrated solution. The precipitate was collected and it was used for further studies (Preethi *et al.* 2023).

3. Results and discussion

3.1. Food waste properties

Characterization of collected food waste samples was done as per ASTM standards. The food waste had a moisture content of 58.62 wt%, ash content of 5.004 wt%, Volatile matter of 10.12 % and fixed carbon of 26.24 wt%, respectively. In a study, the food waste collected from the university dining hall was mixed and subjected to sun drying to remove the unbound moisture from the large quantity of food waste collected. To reduce the bulk volume of the food waste tp processed in the incinerator sun drying was opted over oven drying. The dried food waste was further crushed by ball milling (SPEX 8000M-230 dual mixer mill, 230 V/50 Hz USA) to particle-size 1.4 mm from 80 mm. The required 1.4 mm food waste particles were recovered using a sieve. The food waste comprised volatile matter of 73.78%, ash content of 3.62% and fixed carbon 13%, respectively. Additionally, the food waste had carbon, hydrogen, nitrogen and oxygen content of 45.71, 6.72, 2.91 and 44.66% individually (Dharminder *et al.* 2020). During the experiments, the release of volatile matter at higher temperatures shows higher ash content formation.

3.2. Activated carbon yield

This study produced Activated carbon from food waste to treat biodiesel wash water. Table 1 compares activated carbon yield from food waste at varying normality (0.5 to 3.5 N) and constant temperature of 80 °C, food waste of 0.5 g and time of 120 min. The results showed that the maximum activated carbon yield was 0.33g at 2 N of $ZnCl_2$. The increased activated carbon yield would have been due to the activation of food waste by $ZnCl_2$, respectively. The primary reason for synthesizing and activating food waste-based activated carbon instead of readily available carbon material is to provide an economical and environmentally friendly process for biodiesel wash water treatment. Further, the activated carbon regeneration ability and sodium hydroxide recovery ability of synthesized activated carbon were studied. High temperature-based carbon

material synthesis process favors the porosity generation on the surface and trapping of pollutants present in the wastewater (Prasannamedha *et al.* 2021).

Table 1. Synthesis of food waste activation carbon (2N $ZnCl_2$, 0.5 g of food waste)

Temperature (°C)	Time (Min)	Yield (g)
65	60	0.05
	90	0.14
	120	0.19
70	60	0.15
	90	0.19
	120	0.27
75	60	0.12
	90	0.18
	120	0.27
80	60	0.13
	90	0.19
	120	0.33
85	60	0.18
	90	0.23
	120	0.30
90	60	0.16
	90	0.23
	120	0.31
95	60	0.15
	90	0.31
	120	0.34

3.3. Food waste-based activated carbon characterization

3.3.1. IR-Raman analysis

The Raman spectrum was used to predict the prepared activated carbon's chemical structure and crystalline nature. The IR-Raman analysis of CAC, FWAC, TCAC and WTFAC is shown in Figures 2 and 3. The 514 nm selectively excites the π state of sp^2 hybridized carbon molecules. The obtained Raman peaks in the FWAC sample at 1360 and 1595 cm^{-1} and in the CAC sample at 1340 and 1591 cm^{-1} are indexed to the D and G bands of the graphitic carbon particles. G band represents the vibrational modes arising from the sp^2 hybridized carbon atoms via stretching of the associated bonds. The peaks located at 1595 cm^{-1} and 1591 cm^{-1} for the CAC and FWAC samples correspond to the E2g symmetry modes (G band), thereby confirming the highly crystalline and ordered nature of graphitic carbon. Compared to the G band of graphite around 1575 cm^{-1}, the higher value of peak at 1595 and 1591 cm^{-1} for the G band of FWAC and CAC sample is attributed to the C–C bond bending in the sample due to the porous nature of the FWAC and CAC. The D band observed around 1360 cm^{-1} and 1340 cm^{-1}. After adsorption, the Raman spectroscopy for WTFAC and TCAC 1584 cm^{-1} and 1594 cm^{-1} G band and 1346 cm^{-1} and 1369 cm^{-1} for D band. Similar band pattern was also observed in the activated Carbon Derived from Seed Shells of *Jatropha curcas* for Decontamination of *Zearalenone Mycotoxin* (Kalagatur *et al.* 2017).

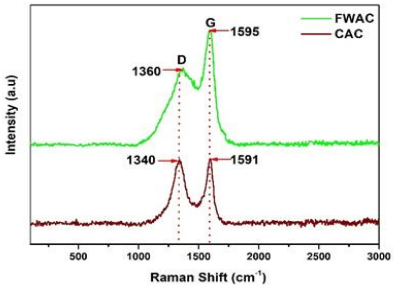


Figure 2. IR-Raman graph of CAC and FWAC

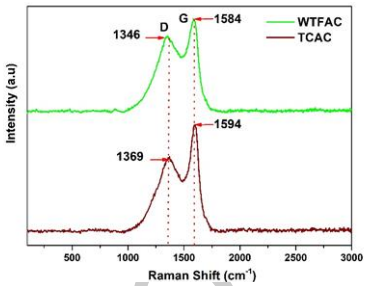


Figure 3. IR-Raman graph of WTFAC and TCAC after adsorption

3.3.2. FESEM

The FESEM analysis of prepared activated carbon was done using a Scanning Electron Microscope (FESEM)-SUPRA 55-Carl Zesiss, Germany. Figures 4 and 5 show the outer surface of CAC, FWAC, TCAC and WTFAC, respectively. The waviness in the surface of the adsorbents would have been due to the lesser degree of roughness on the surface. The carbon material produced from the food waste material showed a low volume of pores, and it is noted for further examination. After the activation process, the pore size volume increased, which was expected from the knowledge gained from the literature survey (Adilakhmi *et al.* 2023). Few discontinuous and rough surface areas were seen, which would have been due to the unavailability or ineffective activation mechanism. Some cylindrical shaped pore surfaces are seen and it was more convincing for the adsorption process to take place. $ZnCl_2$ activation enhanced the presence of micro and macro-sized pores on the surface of the carbon material. In another study, cloth-based activated carbon was activated with $ZnCl_2$ and it showed a highly porous surface area with a more excellent adsorption mechanism (Rakib *et al.* 2020). Another study reported that the SEM image of carbon material before and after the adsorption process revealed the presence of irregular flakes with small strips in the adsorption carbon material. This differed from the carbon material obtained after adsorption (Hua *et al.* 2020).

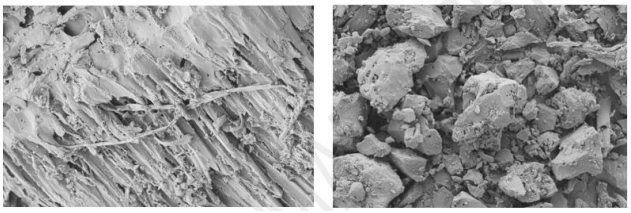


Figure 4. Surface morphology analysis of CAC and FWAC

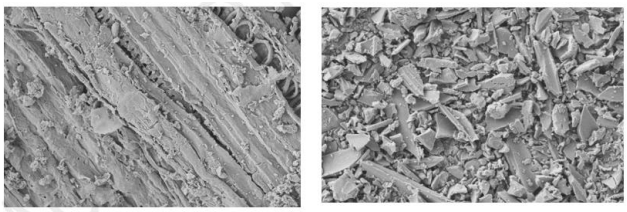


Figure 5. Surface morphology analysis of TCAC and WTFAC after adsorption

3.3.3. XRD analysis of synthesized activated carbon

The crystalline phase of synthesized CAC, FWAC and WTFAC, TCAC was identified from the XRD results (Figures 6 and 7). The obtained diffraction peaks are indexed to the corresponding peaks for FWAC, (002), (100), CAC (002), WTFAC (100), (002) and TCAC (002), (100) crystal planes of graphitic carbon. The average crystallite size of the samples was calculated from the full width at half maximum (FWHM) value of the highly intense peak corresponding to the (002) crystal plane**.** The peak splitting observed in the X-ray diffraction peaks is due to the carbon transition from a highly symmetric phase to a lower one. It was reported that the XRD pattern of activated carbon shows an amorphous nature and revealed the presence of broad peaks corresponding to the nanometric scale (Buscotin *et al.* 2017).

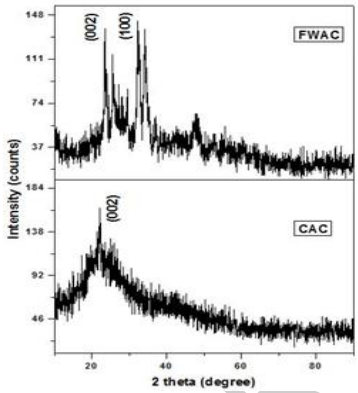


Figure 6. XRD graph pattern of FWAC, CAC

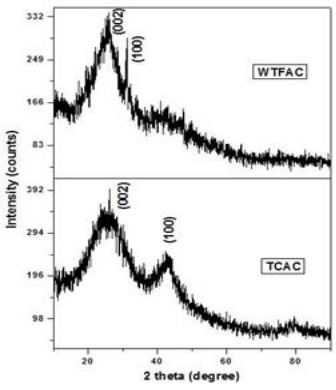


Figure 7. XRD graph pattern of WTFAC, TCAC

3.4. Adsorption studies

3.4.1. Effect of pH

Adsorption experiments were performed to determine the effect of pH of biodiesel wash water and its results are shown in Figures 8 and 9. From Figure 8, it can be seen that the initial pH of the biodiesel washwater was 11.5. The adsorption studies were performed with 0.1 to 0.5g of adsorbent. The results showed that the maximum reduction in pH (7.7) at 30 min was seen when 0.5 g of FWAC was added. The efficiency of the adsorption process depends upon the solution phase and the surface properties of the adsorbents (Dwivedi *et al.* 2014**)** (Sangeetha *et al.* 2023). Figure 9 shows the results of pH reduction in the biodiesel wash water after titration. The results showed that the maximum reduction in pH (7) was seen at the 0.2 g dosage at 30 min of contact time. Lower pH of the solution helps in more excellent removal of pollutants as the adsorbents will have a positively charged surface and attract the negatively charged pollutants. Another study with BR18 by the activated carbon material showed that pH is the most important parameter controlling the protonation and deprotonation process in the adsorbent surface (Mohammed *et al.* 2021).

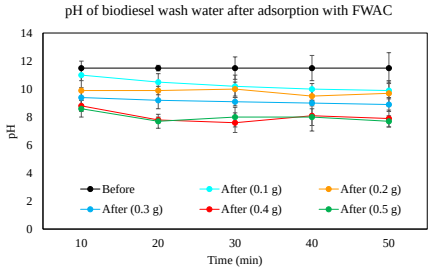


Figure 8. Effect of adsorbent dosage (FWAC) on pH reduction in washwater after the adsorption process

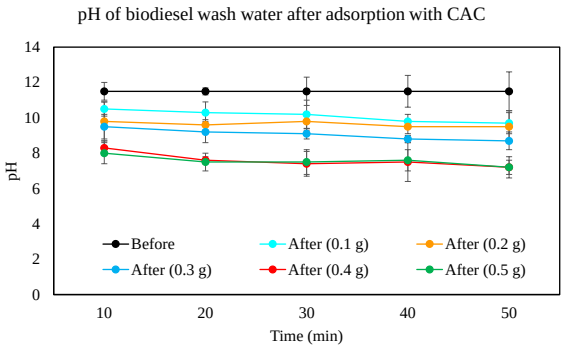


Figure 9. Effect of adsorbent dosage (CAC) on pH reduction in washwater after adsorption process

3.4.2. Effect of TDS

Adsorption experiments were performed to predict the effect of TDS on biodiesel washwater. Figure 10 shows the adsorption effect of food waste-activated carbon in TDS reduction with varying times (0 to 50 min). It was seen that the maximum reduction of TDS was 86 % (TDS was reduced to 145 mg/L from 1140 mg/L) at 10 min with 0.5g of dosage. An increase in time to 50 min has reduced the TDS removal efficiency to 79.5%, respectively. The reduction in the removal of pollutants with an increase in time may be due to the unavailability of active sites of the adsorbents since the pollutants fill the active sites in the initial stage (Pushpraj *et al.* 2019**)**. An increased time and unavailability of free sites helps reduce BOD, COD, pH and other properties. Figure 11 shows the reduction in TDS of wash water after titration. The maximum reduction in TDS was 8.7% at 10 min with 0.1 g of dosage. The initial pH of

washwater was 1040 mg/L and reduced to 285 mg/L after adsorption. Later, it was titrated to recover sodium hydroxide. After titration, the TDS was reduced to 260 mg/L from 285 mg/L, respectively.

3.4.3. Turbidity

Turbidity is the measure of the clearness of water. The presence of dissolved solids in the water medium defines the turbidity of the water. High turbidity is measured when the medium is opaque or turbid. In our study, the turbidity experiments were performed for both CAC and FWAC adsorbents. From the results (Figure 12) of FWAC-based adsorbent studies, it was seen that an increase in time increased the efficiency of the process. The clearness of water increased to 77, 88, 98, 99, and 99% from 58, 72, 79, 90 and 96%, respectively. Here, the turbidity of washwater decreased to 15, 8, 6, 3 and 1 NTU from 435 NTU with 0.5 g of adsorbent dosage after 10, 20, 30, 40 and 50 min, respectively. Turbidity is also the measure of the changes in the suspended solids in a water medium. However, this does not provide the measure of the solids present. This means that the turbidity measures the relative clarity of the solution. Our results (Figure 13) showed that increased time showed higher clearness in water for CAC-based adsorbent studies. Turbidity of washwater decreased to 10, 8, 1, 1 and 1 NTU from 435 NTU with 0.5 g of adsorbent dosage after 10, 20, 30, 40 and 50 min, respectively. Turbidity nature of water showed 68, 77, 85, 90, 97% from 77, 88, 98, 99, 99% for 0.1, 0.2, 0.3, 0.4 and 0.5 g of adsorbent dosage, respectively.

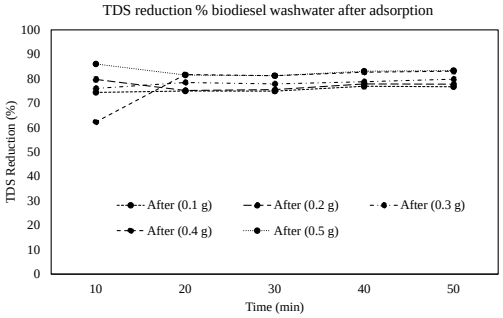


Figure 10. Effect of adsorbent dosage (FWAC) on TDS reduction in wastewater after the adsorption process

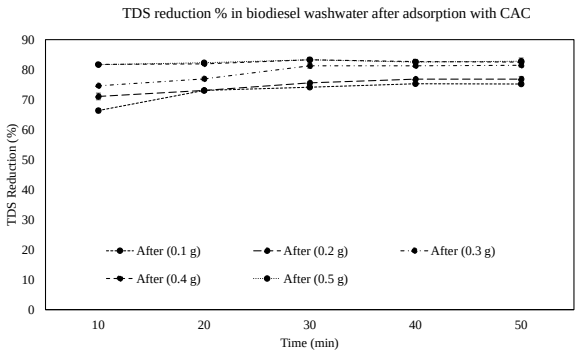


Figure 11. Effect of adsorbent dosage (CAC) on TDS reduction in wastewater after the adsorption process

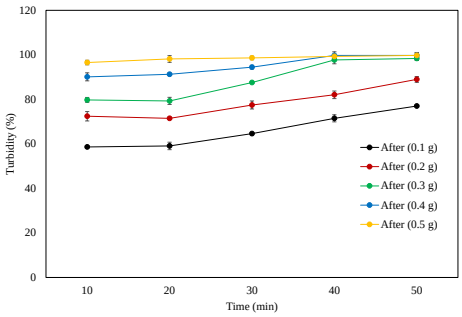


Figure 12. Effect of adsorbent dosage (FWAC) on turbidity reduction in wastewater after the adsorption process

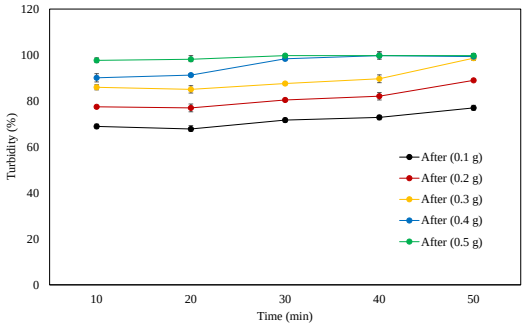


Figure 13. Effect of adsorbent dosage (CAC) on turbidity reduction in wastewater after adsorption process

3.4.4. Feasibility studies for sodium hydroxide recovery from the biodiesel wash water

Washwater was titrated to predict the feasibility of recovering sodium hydroxide from the washwater. Raw washwater and treated washwater were studied in adsorption experiments with both CAC and FWAC. Titration results of FWAC and CAC related to pH and TDS of the studies were shown in Figures 14, 15, 16 and 17, respectively. The results of titration studies performed for the wash water derived from pH studies showed that increased adsorption time resulted in achieving neutrality of the wash water. Washwater obtained from 0.3 g of CAC treated wash water showed neutrality in 20 min of reaction time. Similarly, washwater obtained from 0.2 g of FWAC-treated wash water showed neutrality in 20 min of reaction time. Titration is the chemical analysis of the quantity of constituent and the measure of added known sample to a definite proportion.

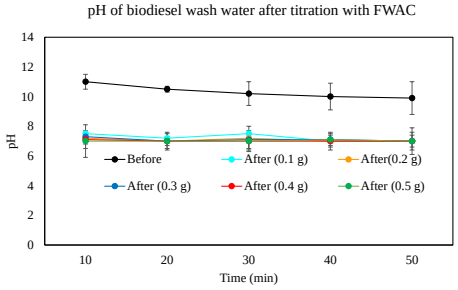


Figure 14. Effect of adsorbent dosage (FWAC) on pH reduction in wastewater after neutralization

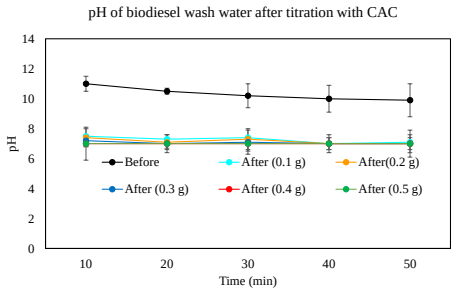


Figure 15. Effect of adsorbent dosage (CAC) on pH reduction in wastewater after neutralization

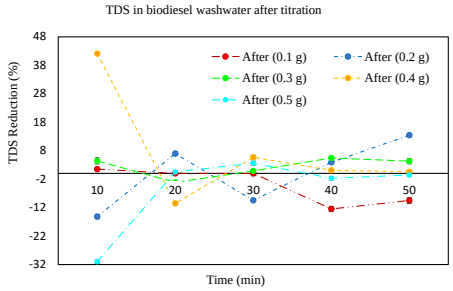


Figure 16. Effect of adsorbent dosage (FWAC) on TDS reduction in wastewater after titration process

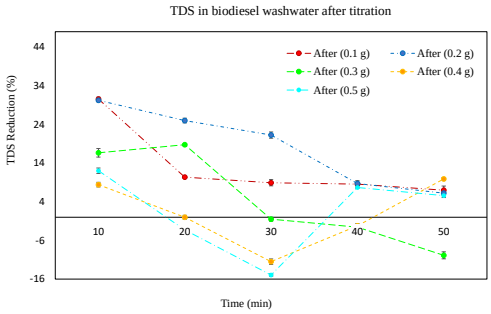


Figure 17. Effect of adsorbent dosage (CAC) on TDS reduction in wastewater after titration process

The TDS of raw washwater before the adsorption process was 1040 mg/L and was reduced to a maximum of 174 mg/L for 0.4g of CAC adsorbent at 30 min of reaction time. TDS has reduced significantly for the 0.1g adsorbent treated samples than higher concentrated washwater samples. A maximum of 30% TDS reduction was seen after titration. Similarly, for FWAC-based adsorbent studies, the TDS has reduced to a maximum of 145 mg/L for 0.5g at 10 min from 1040 mg/L. The titration studies showed a maximum reduction of 42% at 10 min for the 0.4g sample. However, titration studies have also resulted in harmful TDS data, indicating the water solution is unclear. This was attributed to the formation of sodium hydroxide precipitates in the solution.

3.4.5. Recovery of sodium hydroxide (NaOH %)

Recovery of sodium hydroxide helps achieve sustainability in extensive scale processes as recovery and reuse of catalysts will be a more significant achievement on an industrial scale. NaOH recovery is much needed as it will quickly react with other chemicals present in the environment upon improper disposal. After the titration process, the recovery of sodium hydroxide is initiated. The formation of precipitates from the titration process is recovered and its weight is calculated. In some cases, in the absence of precipitate formation, methanol (a solvent) is added to the titrated effluent and later, the agglomerates are collected and the weight is estimated. The sodium hydroxide recovered from the washwater-treated samples (FWAC and CAC) at different experimental conditions is shown in Figures 18 and 19, respectively. The results (CAC-based samples) showed that sodium hydroxide recovery was up to 90% of the total amount of sodium hydroxide present in the washwater. 0.125 N of NaOH was initially used as a catalyst in the 1L transesterification process and washwater. It was found to be 0.06N of NaOH. After titration, the samples obtained from CAC-treated washwater showed a minimum of 0.0038 N in 0.1g treated washwater. This means 93.66% of NaOH in the treated washwater was precipitated and recovered. In another study, through the electrodialysis process, 40% of NaOH was recovered from industrial wastewater using forward osmosis membranes (Babar *et al.* 2015). The role of NaOH in recovering elemental mercury from waste sludge and mixture wastes from a model industrial process that uses a thermal desorption process (Back 2 *et al.* 2020). Chlorination in an alkaline environment can significantly lessen the genotoxic effects of chlorinated waters. (Fang *et al.* 2023)

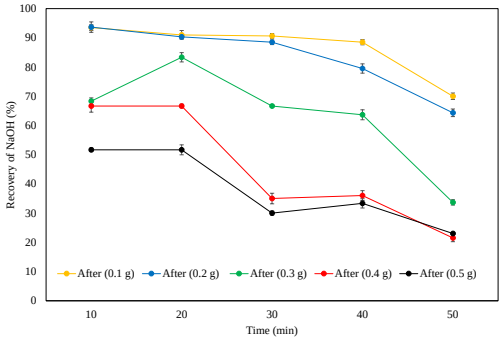


Figure 18. Effect of adsorbent dosage (FWAC) on recovery of sodium hydroxide from washwater after titration process

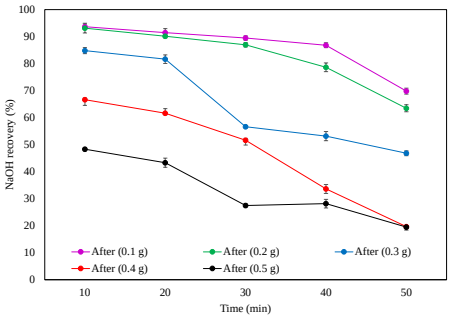


Figure 19. Effect of adsorbent dosage (CAC) on recovery of sodium hydroxide from washwater after titration process

Similarly, for the FWAC-treated samples, variation in the concentration of NaOH was seen owing to the efficiency of the adsorption process. The concentration of NaOH varied from 0.0038 N to 0.047 N in the samples collected from 10 to 50 min and 0.1 to 0.5 g of adsorption experiments. The maximum recovery of NaOH from the adsorption experiments washwater was 93.66% of 0.2g FWAC sample treated washwater at 10 min. At higher concentrations of

adsorbent (0.5g) and at higher adsorption time (50 min), the NaOH recovery percentage was only 23%. Reduction in NaOH recovery at higher concentrations may be attributed to the inability in aggregate formation.

Regeneration of NaOH from an electrochemical study showed recovery of about 50% of NaOH from the process, which in turn was US $ 0.97 per kg of NaOH (Wei *et al.* 2012)**.** Our study used 0.125 N of NaOH (Rs. 0.04) in the 1 L transesterification process. After the adsorption studies, the washwater had 0.06 N NaOH concentration in treated washwater. After the titration process, 0.0039 N was present in the titrated washwater. Hence, around Rs. 0.0012 of NaOH was recovered from the washwater.

4. Conclusion

The low-cost activated carbon from food waste was recommended for treating the highly alkaline and turbid wash water generated during biodiesel production. The food waste based activated carbon was prepared via carbonization and the carbonized food waste was then activated using Zinc Chloride. The 2N $ZnCl_2$ activated carbon was then enhanced to improvise its adsorption properties. The pore size increase was found while comparing the FE-SEM image of before and after activation of $ZnCl_2$ activated carbon derived from food waste. The obtained diffraction peaks are indexed to the corresponding peaks for FWAC, (002), (100), CAC (002), WTFAC (100), (002) and TCAC (002), (100) crystal planes of graphitic carbon. The average crystallite size of the samples was calculated from the full width at half maximum (FWHM) value of the highly intense peak corresponding to the (002) crystal plane**.** The obtained Raman peaks in the FWAC sample at 1360 and 1595 cm^{-1} and in the CAC sample at 1340 and 1591 cm^{-1} are indexed to the D and G bands of the graphitic carbon particles. The peaks located at 1595 cm^{-1} and 1591 cm^{-1} for the CAC and FWAC samples correspond to the E2g symmetry modes (G band), thereby confirming the highly crystalline and ordered nature of graphitic carbon. After adsorption, the Raman spectroscopy for WTFAC and TCAC 1584 cm^{-1} and 1594 cm^{-1} G band and 1346 cm^{-1} and 1369 cm^{-1} for D band. The biodiesel washwater generated during biodiesel refining was treated with the synthesized FWAC. Adsorption experiments were conducted at varying times and FWAC dosages. The reduction in pH, turbidity and TDS from 11.5 to 7, 435 NTU to 1NTU and 1140 ml/L have proved FWAC to be a promising adsorbent for highly alkaline and turbid waters like biodiesel wash water. The study also paves the way for new ventures to recover sodium hydroxide from the biodiesel washwater, enabling economic and environmental sustainability for the industries involved in biodiesel production.

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Conflict of Interest

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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