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Original Research Article

Use of Agrowastes Biosorbents for Treatment of Refinery Wastewater

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Abstract

Refinery wastewater has been causing environmental pollution with serious adverse health effects and environmental destruction. This study aims at evaluating the capacity of cassava peels and sugarcane bagasse biosorbents in removing heavy metals, and organic pollutants from the oil refinery wastewater. The proximate and minerals composition of the cassava peels (CP) and sugarcane bagasse (SCB) was determined using the method of AOAC. The pH, turbidity, biological oxygen demand (BOD), and chemical oxygen demand (COD) were determined using digital pH meter, turbidity meter, 5-Day BOD test, and colorimetric technique, respectively. The heavy metals, phenol, and total oil and grease (TOG) content was estimated using AAS and colorimetric method of AOAC. Batch adsorption test was conducted using completely mixed batch reactors (CMBR) method. The results showed that CP and SCB contain significant ($p < 0.05$) amount of ash (5.38 %, 2.15 %), fiber (20.63 %, 3.83 %), carbohydrate (7.87 %, 27.64 %), proteins (1.87 %, 1.42 %), moisture (1.20 %, 14.99 %), and lipids (2.52 %, 4.22 %), respectively. The CP (3.72mg/100g, 5.41mg/100g, 8.1mg/100g, 3.00mg/100g, 6.52mg/100g, and 4.26mg/100g) contain high significant ($p < 0.05$) amount of sodium, potassium, calcium, iron, zinc, and copper compared with that of the SCB (2.33mg/100g, 2.10 mg/100g, 5.40mg/100g, 1.88mg/100g, 2.09mg/100g, and 2.14mg/100g), respectively. The pH value of the wastewater sample treated with the biosorbents was significantly ($p < 0.05$) high compared with the pH value of the untreated wastewater sample. At significant ($p < 0.05$) reduction in turbidity, COD, and BOD was observed in the wastewater sample treated with combination of the biosorbents compared with the untreated wastewater. The wastewater sample treated with combination of the biosorbents demonstrated significant ($p < 0.05$) decreased in phenol and TOG content compared with the untreated wastewater. The biosorbents exhibited high removal efficiency against cadmium, lead, nickel, and chromium up to 65.70 %, 80.30 %, 52.46 %, and 72.70 %, respectively. The biosorbents displayed a methylene blue and Congo red dye removal efficiency of 85.66 % and 74.23 %, respectively. The R^2 value of lead, cadmium, nickel, chromium, methylene blue and congo red dye for Langmuir isotherm model is higher than that for Freundlich isotherm model. Thus, the experimental equilibrium data for heavy metals and the dyes were best fitted to the Langmuir model than the Freundlich model.

Keywords: Agro-wastes, Cassava peels, Sugarcane bagasse, Oil refinery, Wastewater.

INTRODUCTION

Over two billion people lack access to safe and affordable drinking water, and more than 57% of the world's population expects to have difficulty in accessing safe and drinkable water by 2050 (WHO, 2020). Pollution due to refinery wastewater disposal remains a major environmental challenge causing adverse health effects and environmental impacts. The presence of several pollutants, including oil and grease, toxic organic compounds, ammonia, phenol and suspended solids make oil refinery wastewater a severe environmental pollution source (Zhao *et al.,* 2024; Tetteh and Rathilal, 2020). Demand for sustainable solutions for the treatment of refinery wastewater in oil and gas industry has been increased. Conventional treatment methods are ineffectively applicable in removing complex organic pollutants from the wastewater. Conventional treatment techniques are not applicable or effective in certain societal segments due to their limitations which include specificity, production of large amounts of toxic sludge, and high capital costs. Thus, there is need for developing an effective, sustainable, less expensive, and efficient solution for treating oil and gas refinery wastewater.

Adsorption is an effective treatment technique and has many advantages including simplicity, easy operation, affordability, adaptability, and high absorption capacities (Sardar *et al.,* 2021; Tiwari *et al.,* 2021; Dai *et al.,* 2018). Agro-waste materials are abundantly available in several communities in the world and have high efficiency for removing various pollutants due to their complex chemical composition. Agro-wastes are leftover parts of plants after processing and include husks, leaves, stems, roots, and outer skin (Tiwari *et al.,* 2021). Agro-waste adsorbents have been used in treatment of refinery wastewater contaminated with hydrocarbons, heavy metals, and organic pollutants (Smith *et al.,* 2020). The physicochemical characteristics of the agro-wastes make them a very good biosorbents for removing pollutants from wastewater (Sardar *et al.,* 2021).

Cassava peels are one of the materials that can be utilized as an alternative due to its availability to assist the production of biosorbents (Kayiwa *et al.,* 2021). Cassava peels have the potential to be used as an adhesive in the production of many biosorbents due to their high moisture content, volatile materials, ash content, fixed carbon content, lignin content, cellulose content, hemicellulose content, and calorific value (Kayiwa *et al.,* 2021; Hirniah, 2020). Sugarcane bagasse is an effective agro-waste with significant potential for removal of heavy metals and other pollutants from the wastewater (Kumar *et al.,* 2019). Raw, carbonized, or chemically modified forms of sugarcane bagasse have been used for treatment of wastewater due to its capability for adsorbing metal ions (Ezeonuegbu *et al.,* 2021). This study aims at evaluating the efficacy of cassava peels and sugarcane bagasse biosorbents in removing heavy metals, and organic contaminants from the oil refinery wastewater.

MATERIALS AND METHODS

Study Area

This study was conducted using the waste water sample from Indoroma Eleme Petrochemicals ltd, Port-Hacourt, Rivers State, Nigeria. The experiments were carried out in Science Laboratory Technology Laboratory and ACE Fuels Laboratory, Federal University of Technology, Owerri, Imo, Nigeria. Indorama Eleme Petrochemicals Limited is an olefin-based multi-petrochemical complex with liquid natural gas as its main feed-stock. The company is located at East-West Express Way, Eleme, Port Harcourt, Rivers State Nigeria. The area is located on Latitude 4˚50'8"N and Longitude 7˚6'11"E. Indorama Eleme Petrochemicals complex site is spatially approximately between l0km North-East of Port Harcourt, the capital city of Rivers State of Nigeria and 40km South-West of the largest commercial Town, Aba in Abia State, Nigeria.

Collection of Samples

The oil refinery waste water sample was collected from Eleme Petrochemicals, Port-Hacourt, Rivers State, Nigeria. The water sample was collected using clean and dried plastic cans from the surface to a depth of about 15 – 20 cm at three different locations. After being collected, the geographical locations of each location were recorded. All water samples were appropriately labeled and then transported to the Post Graduate Laboratory, Department of Biotechnology, Federal University of Technology, Owerri, Imo, Nigeria. The agro-wastes (cassava peels and sugarcane bagasse) were collected from the milling local vendors in Owerri, Imo, Nigeria in clean sample containers.

Preparation of the Agro-wastes

The agro-wastes (cassava peels and sugarcane bagasse) were thoroughly washed with distilled water to remove the remove dust and impurities. The washed samples were air dried for 12 hours and then oven-dried to a constant weight at 65 °C for 36 hours. The dried samples were cut into bits, and mashed using pestle and mortar to soften them and later ground into semi-fine particles. The materials were sieved using 500 µm sieve to obtain homogenous particle sizes. The samples were then washed thoroughly with distilled water to remove any unwanted matter introduced during the crushing process. The washed samples were then placed in an oven maintained at 105 ºC for 12 hours for moisture removal. The dried samples (500 g) were measured and introduced into the hot zone of the muffle furnace for 120 minutes at 380 ºC. The carbon formed was allowed to cool for 5 hours at room temperature. The carbon samples were stored in clean sample containers and labeled appropriately until further analysis.

Determination of Proximate Composition of the Agro-wastes

The analysis of crude lipid, moisture, carbohydrate, crude protein, ash and fiber content of the cassava peels and sugarcane bagasse was carried out using the method of AOAC (2010) and Aliyu *et al.* (2025). The experiments were conducted in triplicate and the average value of the data was obtained. The results were expressed in percentages as the mean and SEM.

Determination of Minerals Composition of the Agro-wastes

The level of calcium, iron, zinc, copper, magnesium, and manganese in the cassava peels and sugarcane bagasse were determined by atomic absorption spectrophotometeric technique using the method of AOAC (1990) and Aliyu *et al.* (2025). The concentration of sodium and potassium content of the cassava peels and sugarcane bagasse was estimated using flame photometeric technique as described by AOAC (1990). The concentration of phosphorus in the cassava peels and sugarcane bagasse was determined using spectrophotometeric method as described by Aliyu *et al.* (2025).

Determination of Physicochemical Properties of the Wastewater

Determination of pH

The pH value of the refinery wastewater sample was determined using digital pH meter. The pH values were measured and recorded in triplicate and the average value was calculated.

Determination of Turbidity

The turbidity of the refinery wastewater sample was used measured in Nephelometric Turbidity Unit (NTU) using digital turbidity meter. The values were measured three times and the mean value was obtained.

Determination of Biological Oxygen Demand

The biological oxygen demand (BOD) of the refinery wastewater sample was estimated using 5-Day BOD Test dilution method. Two hundred miles of the wastewater was overflowed in a airtight bottle. The dissolved oxygen of the wastewater sample was first measured using the Schott Gerate Dissolved Oxygen meter. The wastewater sample was incubated at 20 ^{0}C for 5 days and then the dissolved oxygen of the water sample was measured after the 5 days period. The dissolved oxygen values were measured in triplicate and then the BDO of the wastewater sample was obtained using the following equation:

BOD_5 (mg/L) = $[DO_1 - DO_0]/ B$

Where; DO_0 is initial dissolved oxygen, DO_1 is final dissolved oxygen, B is volume of the wastewater sample used.

Determination of Chemical Oxygen Demand

The chemical oxygen demand (COD) of the refinery wastewater sample was evaluated using colorimetric technique according to the method described by ASTM (2011) and APHA (2005). The COD vial adapter was placed in the cell holder of the spectrophotometer. A blank reagent was used to zero the spectrophotometer. The wastewater sample (10 L) was measured into the vial placed in the adapter. The absorbance was read at 520 nm wavelength and the concentration was obtained from the standard curve. The COD values were measured and recorded in triplicate and the average value was obtained.

Determination of Total Oil and Grease

Colorimetric method was used for the analysis of total oil and grease (TOG) content of the water sample as described by Cirne *et al.* (2016). Forty mile of the water sample was treated with 50 ml of n-hexane. The extract was filtered through a filter paper containing anhydrous sodium sulfate (10 g) and then collected in a 100 ml flask. Calibration curve was constructed using oil and grease prepared solution at 5, 25, 50, 100 and 200 ppm. Absorbance of the sample was measured using colorimeter at 400 nm wavelength. The concentration of oil and grease was obtained from the standard curve. The experiment was carried out in triplicate and the average value was calculated.

Determination of Heavy Metals Content

The levels of lead, nickel, chromium, and cadmium in the oil refinery wastewater sample were determined using atomic absorption spectrophotometer according to the method of AOAC (2005) and Abubakar *et al.* (2025). The water sample (100 mL) in conical flask was treated with 1 ml of concentrated HNO_3 and 2 - 3 g of anti-bump. The contents were heated for about 5 minutes, allowed to cool and then filtered. Calibration analysis was carried out by diluting 1000 mg/L stock solution of the metals. A minimum of three standard working solutions ranged between 0.1 mg/L to 10 mg/L were prepared from the stocks. External calibration was used by running de-ionized water and a suit of calibration standards for each metal. Absorbance of each of the metal was measured at a specified wavelength. The concentrations of the metals were obtained from their respective calibration curves.

Activation of the Agro-Wastes Carbon

The agro-wastes carbon was activated using the method of Thompson *et al.* (2020) and Behnood *et al.* (2016). One hundred grams of agro-wastes carbon were treated with 0.5 g of stearic acid in 200 mL of n-hexane containing two to three drops of concentrated sulphuric acid as catalyst. The contents were refluxed in dean stark apparatus at 65± 2 ◦C for 4 hours ant then treated with n-hexane followed by excess distilled water until neutral pH was achieved. The treated adsorbents were oven dried at 110 ℃ for 4 hours. The dried adsorbents were pulverized to fine powder using a mortar and pestle and sieved using 100 μm mesh. The Biosorbents were store until further analysis.

Biosorption Test

The cassava peel (CP) and sugarcane bagasse (SCB) activated carbons were packed in a separate three fixed, equal size adsorption columns. The oil refinery wastewater was placed in a plastic container with its outlet connected to the three adsorption columns by means of valves. The valves were opened to allow equal volume of wastewater through the three adsorption columns by gravity. Distilled water was passed through the columns to wet the activated carbon bed before the experiment. The effluents were collected from the three flasks analyzed at 3 hours interval for 9 hours and triplicate reading of the adsorption parameters were obtained. The physicochemical properties and heavy metals contents of the treated and untreated refinery wastewater were analyzed.

Batch Adsorption Study

Batch adsorption study was conducted to evaluate the efficiency of adsorption of oil pollutants particularly phenol, total oil and gas, and heavy metals in the oil refinery wastewater by the agro-wastes activated carbon. The test was performed using the method of Oghenejoboh *et al.* (2008). Each of the agro-wastes activated carbon (5 mg) was transferred into a glass centrifuge tube in completely mixed batch reactors (CMBR). Fifteen miles of the refinery wastewater were added into the CMBR's tubes and then closed with open closure and sealed with Teflon-lined silicone septa. The oil concentrations 20, 40, 60, 80 and 100 mg/L were prepared from the initial stock of 120 mg/L of the oil. The contents in the tubes were agitated with vortex mixer and allowed to attain to equilibrium at room temperature for 12 hours. After the 12 hours equilibration period, the tubes were then centrifuged at 2500 rpm for 30 minutes to separate the solid and liquid phase. A 100 µL aliquot was removed from each tube and transferred to 5 mL vial for spectrophotometeric analysis. The absorbance for each aliquot was measured using spectrophotometer at 450 nm and the equilibrium concentration was obtained from the prepared calibration curve. The adsorption capacity (q_e) of the agro-wastes activated carbon was estimated using the equation as follow:

$q_e = V/M\,(C_o - C_e)$

The percentage removal efficiency of the agro-wastes activated carbon was calculated according to the equation described by Banerjee *et al.* (2006) and Cheenmatchaya and Kungwakunakorn (2014) as follow:

$\%\ \text{Removal efficiency} = (C_o - C_e) / C_o \times 100$

Where; qe is the adsorption capacity of the activated carbon (mg/g), C_o is the initial concentration of pollutant in the wastewater (mg/L), V is the volume of wastwater used (cm^3), M is the mass of activated carbon used (g).

The data obtained from the batch adsorption experiment were fit into Langmuir isotherm and Freundlich isotherm models in order to find the model that best describe the sorption process and prove the authenticity of the adsorbent produced. The models' equations are:

The Langmuir equation is:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{1}{q_m} C_e$$

Where; C_e is equilibrium concentration (mg/L), q_e is the amount of adsorbed substance at equilibrium (mg/g), q_m is maximum monolayer adsorption capacity (mg/g), and K_L is Langmuir constant related to the energy of adsorption (L/mg) (Adekunle *et al.,* 2023).

The Freundlich equation is:

$$\ln(q_e) = \ln(K_F) + \frac{1}{n}\ln(C_e)$$

Where; C_e is equilibrium concentration (mg/L), q_e is the amount of adsorbed substance at equilibrium (mg/g), K_F is Freundlich constant related to adsorption capacity and n is Freundlich exponent related to adsorption intensity (Egbosiuba *et al.,* 2021).

Statistical Analysis

The experiments were conducted in triplicate and the results obtained were statistically using One-Way Analysis of Variance (ANOVA) using SPSS version 21. The significant differences among the mean values were determined using Dunnet multiple comparison test at 95 % confidence level. Two-tailed ($p < 0.05$) value was considered significance

RESULTS

Proximate Composition of the Agro-Waste Samples

Figure 1 shows the proximate composition of cassava peel and sugarcane bagasse. A significant ($p < 0.05$) amount of ash was observed in CP (5.38 %) compared with SCB (2.15 %). The amount of fiber observed in CP (20.63 %) was significantly ($p < 0.05$) high than that found in SCB (3.83 %). The SCB (27.64 %) demonstrated high significant ($p < 0.05$) amount of carbohydrate compared with CP (7.87 %). The amount of proteins found in CP and SCB was 1.87 % and 1.42 %, respectively. The result showed that the moisture content of SCB (14.99 %) was significantly ($p < 0.05$) high than that of CP (1.20 %). The SCB (4.22 %) exhibited high significant ($p < 0.05$) amount of lipids compared with that observed in CP (2.52 %) (Figure 1).

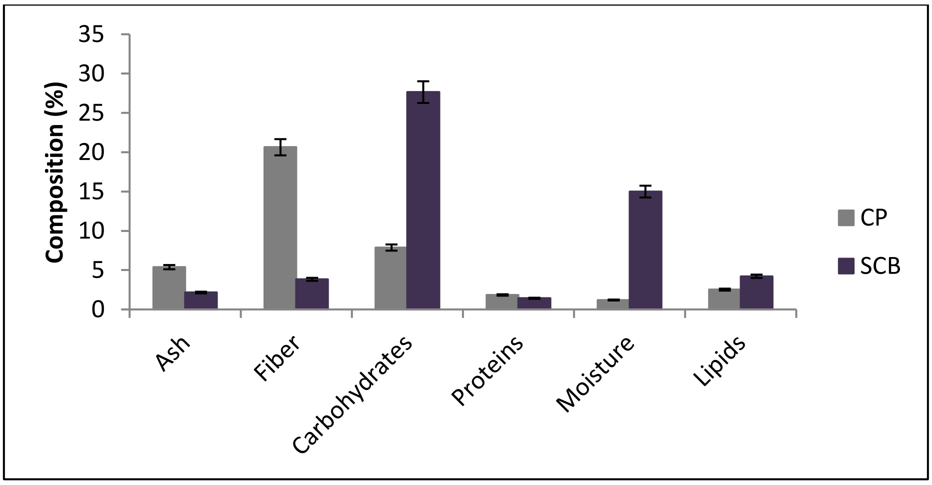

Figure 1: Proximate Composition of the Agro-Waste Samples

Results are expressed as mean ± SEM (n = 3).

Minerals Contents of the Agro-Waste Samples

The minerals content of cassava peel (CP) and sugarcane bagasse (SCB) is shown in Figure 2. The result showed that CP (3.72mg/100g, 5.41mg/100g, 8.1mg/100g, 3.00mg/100g, 6.52mg/100g, and 4.26mg/100g) contain high significant ($p < 0.05$) amount of sodium, potassium, calcium, iron, zinc, and copper compared with that of the SCB (2.33mg/100g, 2.10 mg/100g, 5.40mg/100g, 1.88mg/100g, 2.09mg/100g, and 2.14mg/100g), respectively. However, there was no significant ($p > 0.05$) changes observed in the amount of magnesium, phosphorus, and manganese among the agro-wastes (Figure 2).

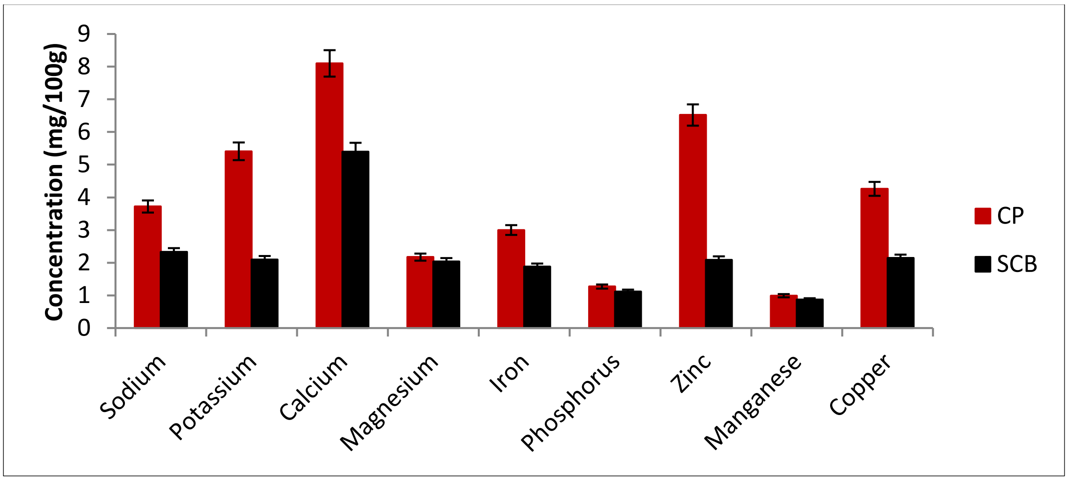

Figure 2: Minerals Contents of the Agro-Waste Samples

Values are expressed as mean ± SEM (n = 3).

Effect of the Biosorbents on Physicochemical Properties of the Oil Refinery Wastewater

Table 1 shows the effect of combination of the cassava peel (CP) and sugarcane bagasse (SCB) biosorbents on pH, turbidity, COD, and BOD of the oil refinery wastewater. The result showed that the pH value of the wastewater sample treated with combination of the biosorbents was significantly ($p < 0.05$) high compared with the pH value of the untreated wastewater sample. The increase in pH value of the treated wastewater sample was in concentration dependent manner. At 25 g/L, the pH value of the treated wastewater sample was high than the pH value observed at 5 g/L, 10 g/L, 15 g/L, and 20 g/L (Table 1). At all the concentrations, a significant ($p < 0.05$) reduction in turbidity, COD, and BOD was observed in the wastewater sample treated with combination of the biosorbents compared with the untreated wastewater. However, more significant ($p < 0.05$) reduction in turbidity value of the treated wastewater was observed at 25 g/L then at 20 g/L, 15 g/L, 10 g/L, and 5 g/L (Table 1).

Table 1: Effect of the Biosorbents on Physicochemical Properties of the Refinery Wastewater

Treatment	pH	Turbidity (NTU)	COD (mg/dL)	BOD (mg/dL)
Control	5.03 ± 0.14^{c}	58.33 ± 0.88^{a}	372.00 ± 0.91^{a}	52.76 ± 0.35^{a}
CP + SB (5 g/L)	5.96 ± 0.14$^{b, c}$	44.66 ± 0.88^{b}	145.33 ± 0.88^{b}	26.76 ± 0.49^{b}
CP + SB (10 g/L)	6.10 ± 0.17$^{a, b}$	43.33 ± 0.45^{b}	144.33 ± 0.21^{b}	25.96 ± 0.48^{b}
CP + SB (15 g/L)	6.23 ± 0.08$^{a, b}$	42.00 ± 0.15^{b}	140.33 ± 0.87^{c}	25.30 ± 0.26^{b}
CP + SB (20 g/L)	6.40 ± 0.05$^{a, b}$	38.66 ± 0.78^{c}	138.33 ± 0.58^{d}	24.66 ± 0.40^{b}
CP + SB (25 g/L)	6.50 ± 0.05$^{a, b}$	36.66 ± 0.68^{d}	136.33 ± 0.45^{e}	24.06 ± 0.31^{b}

Data are expressed as mean ± SEM (n = 3). Values in the same column with different letters are significantly ($p < 0.05$) different.

Effect of the Biosorbents on Phenol and Total Oil and Grease Content of the Oil Refinery Wastewater

The effect of combination of the cassava peel (CP) and sugarcane bagasse (SCB) biosorbents on phenol and TOG content of the oil refinery wastewater is presented in Table 2. The wastewater sample treated with combination of the biosorbents demonstrated significant ($p < 0.05$) dose dependent decreased in phenol and TOG content of the wastewater compared with the untreated wastewater. Treatment of the wastewater with the biosorbents displayed more significant ($p < 0.05$) decrease in the phenol and TOG level at 25 g/L than at 20 g/L, 15 g/L, 10 g/L, and 5 g/L (Table 2).

Table 2: Effect of the Biosorbents on Phenol and Total Oil and Grease Content of the Oil Refinery Wastewater

Treatment	Phenol	TOG
Control	20.13 ± 0.20[a]	63.23 ± 0.49[a]
CP + SB (5 g/L)	8.33 ± 0.23[b]	23.03 ± 0.40[b]
CP + SB (10 g/L)	8.20 ± 0.15[b]	22.80 ± 0.36[b,c]
CP + SB (15 g/L)	7.76 ± 0.23[b]	22.10 ± 0.15[b,c]
CP + SB (20 g/L)	7.26 ± 0.14[b]	21.90 ± 0.11[c]
CP + SB (25 g/L)	7.00 ± 0.17[b]	21.63 ± 0.23[c]

Results are expressed as mean ± SEM (n = 3). Values in the same column with different letters are significantly ($p < 0.05$) different

Heavy Metals Removal Efficiency of the Biosorbents

The heavy metals percentage removal efficiency of combination of the cassava peel (CP) and sugarcane bagasse (SCB) biosorbents is presented in Figure 3. The percentage removal efficiency of the biosorbents against lead, cadmium, nickel, and chromium was 65.70 %, 80.30 %, 52.46 %, and 72.70 %, respectively. This indicated the biosorbents exhibited high removal efficiency against cadmium than the lead, nickel, and chromium (Figure 3).

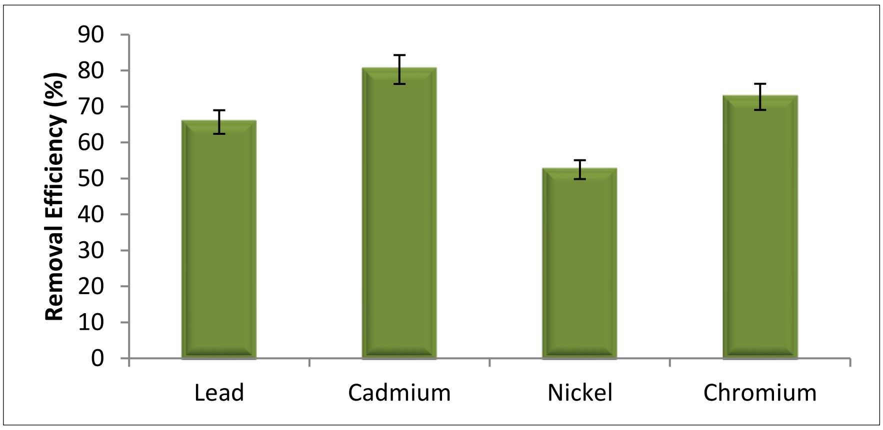

Figure 3: Heavy Metals Removal Efficiency of the Biosorbents Values are expressed as mean ± SEM (n = 3)

Dyes Removal Efficiency of the Biosorbents

Figure 4 shows the percentage removal efficiency of combination of the cassava peel (CP) and sugarcane bagasse (SCB) biosorbents against methylene blue and Congo red dye. The result revealed that the biosorbents displayed a methylene blue and Congo red dye removal efficiency of 85.66 % and 74.23 %, respectively. This showed that the biosorbents exhibited more significant ($p < 0.05$) removal efficiency against the methylene blue than the Congo red dye (Figure 4).

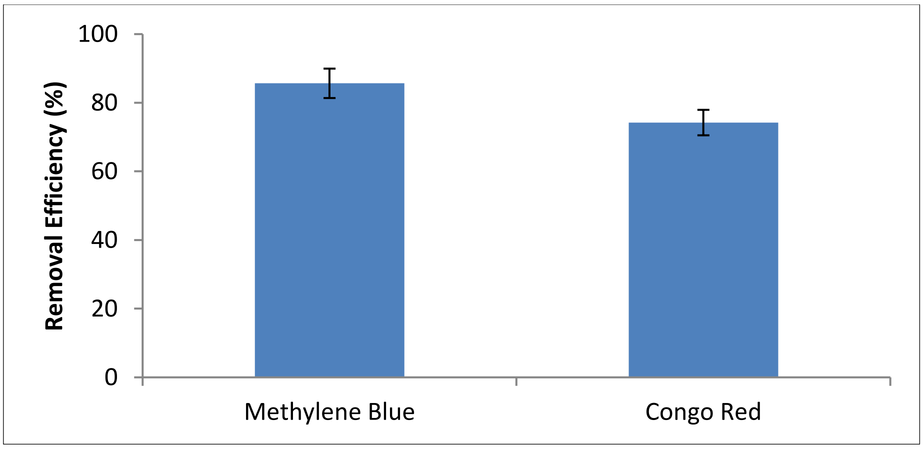

Figure 4: Dyes Removal Efficiency of the Biosorbents Values are expressed as mean ± SEM (n = 3)

Adsorption Isotherms of Heavy Metals and Dyes by the CP and SCB Biosorbents

The graphical representations of plots of the Freundlich model for adsorption of lead, cadmium, nickel, chromium, methylene blue and congo red dye by the cassava peel and sugarcane bagasse biosorbents is shown in Figure 5.

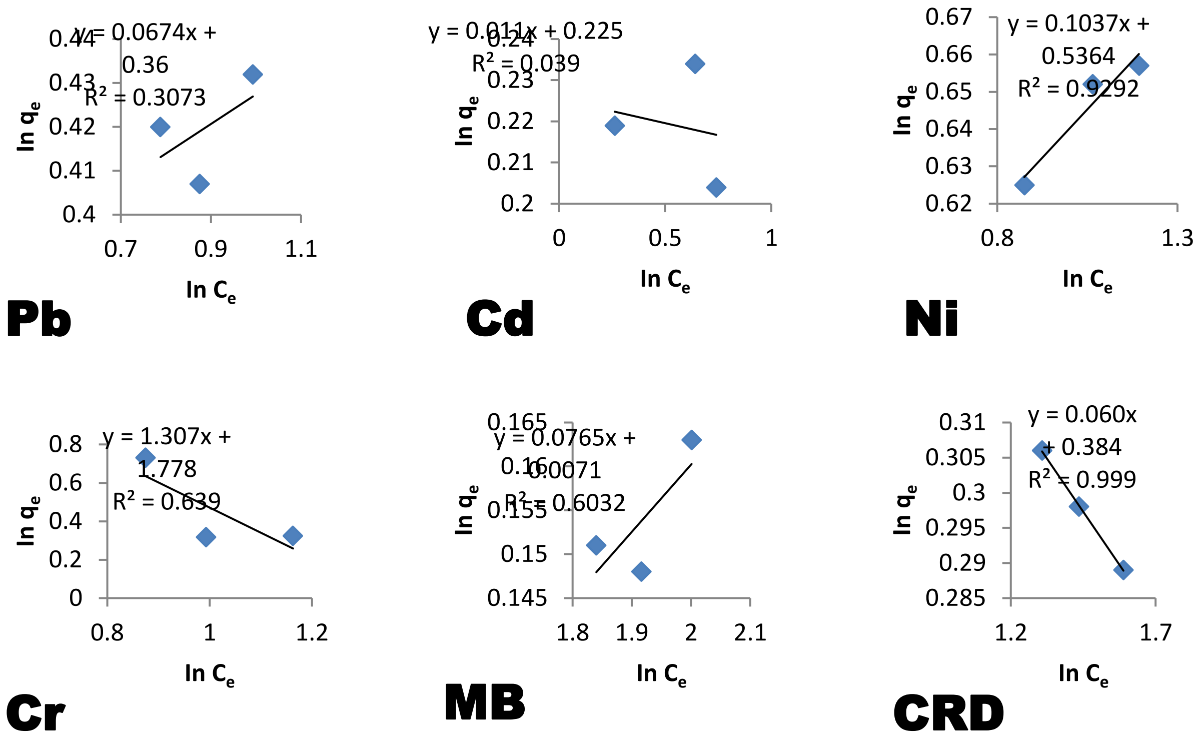

Figure 5: Plots of Freundlich Model for Adsorption of Heavy Metals and Dyes Methylene Blue (MB), Congo Red Dye (CRD)

Table 3 shows the Freundlich constant parameters for the adsorption of lead, cadmium, nickel, chromium, methylene blue and congo red dye by the cassava peel and sugarcane bagasse biosorbents. The constant value n for cadmium (90.909) was higher than that for lead, nickel, and chromium, methylene blue and congo red dye. Chromium displayed high value of K_F (5.918) than the lead, cadmium, nickel, methylene blue and congo red dye. The R^2 value (0.999) of the congo red dye was higher than of the lead, cadmium, nickel, chromium, methylene blue (Table 3).

Table 3: Freundlich Isotherm Constant Parameters for Adsorption of Heavy Metals and Dyes

Heavy Metal	Freundlich Isotherm Constant Parameters		
	n	K_F	R^2
Lead	14.920	1.433	0.307
Cadmium	90.909	1.252	0.039
Nickel	9.708	1.709	0.929
Chromium	0.765	5.918	0.639
Methylene Blue	13.157	1.007	0.603
Congo Red Dye	16.666	1.468	0.999

Figure 6 shows the graphs of Langmuir model for the adsorption of lead, cadmium, nickel, chromium, methylene blue and congo red dye by the by the cassava peel and sugarcane bagasse biosorbents.

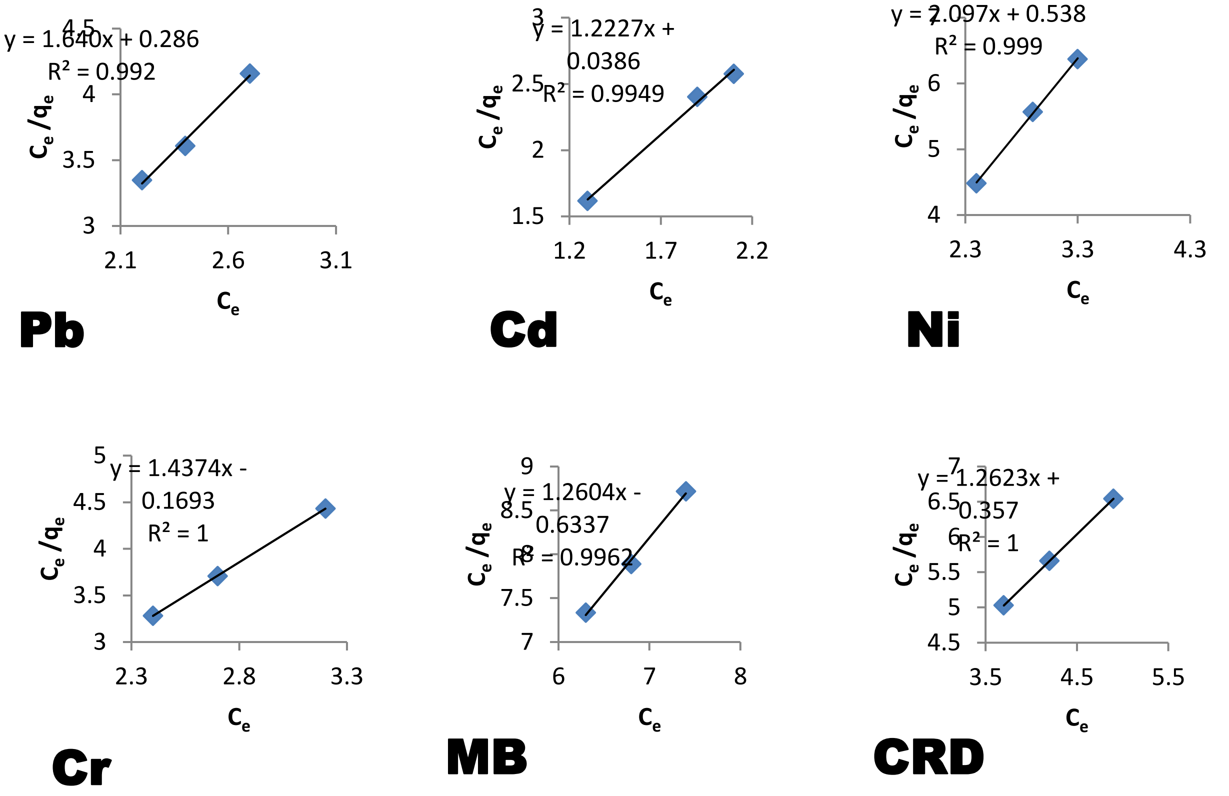

Figure 6: Graphs of Langmuir Model for Adsorption of Heavy Metals and Dyes Methylene Blue (MB), Congo Red Dye (CRD)

The Langmuir constant parameters for adsorption of lead, cadmium, nickel, chromium, methylene blue and congo red dye by the by the cassava peel and sugarcane bagasse biosorbents are presented in Table 4. Cadmium exhibited higher value of q_m (0.818) and K_L (32.258) compared with that of lead, nickel, chromium, methylene blue and congo red dye. Chromium and congo red dye displayed high value of R^2 up to 1 compared with that of lead, cadmium, nickel, and methylene blue (Table 4).

Table 4: Langmuir Isotherm Constant Parameters for Adsorption of Heavy Metals and Dyes

Heavy Metal	Langmuir Isotherm Constant Parameters		
	q_m	K_L	R^2
Lead	0.609	5.747	0.992
Cadmium	0.818	32.258	0.994
Nickel	0.476	3.906	0.999
Chromium	0.695	8.547	1.000
Methylene Blue	0.793	1.996	0.996
Congo Red Dye	0.792	3.546	1.000

From the results, it observed that the R^2 value of lead, cadmium, nickel, chromium, methylene blue and congo red dye for Langmuir isotherm model is higher than that for Freundlich isotherm model. Thus, the experimental equilibrium data for lead, cadmium, nickel, chromium, methylene blue and congo red dye were best fitted to the Langmuir model than the Freundlich model.

DISCUSSION

In this study, the pH value of the wastewater treated with combination of the biosorbents increased in concentration dependent manner. Biosorption capacity reduces with low pH values and increases with pH until it reaches optimum pH (Alfarra *et al.,* 2014). Study showed that the affinity of metal ions present in the oil polluted water is strongly dependent on the solution pH (Alfarra *et al.,* 2014). It has been reported that metal ions are being readily absorbed due to the high concentration of hydroxyl anions in the solution when the pH was greater than 5.5 (Babayemi *et al.,* 2019). In the present study, the oil refinery wastewater treated with combination of the biosorbents demonstrated significant decrease in turbidity, COD, and BOD value. Agricultural wastes have been used for the reduction of COD and

BOD in wastewater and polluted soil (Babayemi *et al.,* 2019).

Result of the current study, indicated that the level of phenol and oil and grease in the oil refinery wastewater treated with combination of the biosorbents was significantly reduced. Agro-wastes have been used for the removal of oil and grease and many organic compounds such as phenol, lignin, bisphenol A, clofibric acid, carbamazepine, naproxen, diclofenac, pyridine, and quinoline (Babayemi *et al.,* 2019). In the present finding, the removal efficiency of combination of the biosorbents increased with increased in the adsorbent's concentration. Similar studies reported that the removal efficiency of agro-wastes against organic pollutants increases along with the increase in the adsorbent dose (Ngulube *et al.,* 2017; Dawood *et al.,* 2014). However, as the adsorbents dose increased, the removal percentage of organic pollutants increases rapidly (Ahmad and Danish, 2022). Relevant research showed that agro-wastes such as peels, bark, husk, leaves, seeds, and straw displayed different adsorptive capacities against organic pollutants and heavy metal ion at high, medium, and low adsorbent doses (Shaukat *et al.,* 2022).

In this study, the oil refinery wastewater treated with combination of the biosorbents demonstrated significant percentage removal efficiency against cadmium, lead, chromium, and nickel. Several studies have shown the usefulness of the agro-waste adsorbents under experimental conditions for removal of metal ions including Cd, Pb, and Cr (Babayemi *et al.,* 2019; Caccin *et al.,* 2016). Agro-wastes have tendency to bind heavy metals due to their high proximate and minerals content containing polar functional groups (Alalwan *et al.,* 2020; Ahmad and Zaidi, 2020). The functional groups in agro-wastes form complexes with metal ions by donating a lone pair of electrons (Ahmad and Zaidi, 2020). Heavy metals can produce adverse effects on human and animals' health and the environment. High level of heavy metals in foods and plants causes toxic effect on certain organs and tissues (Abubakar *et al.,* 2022). Consumption of heavy metals in foods and plants can cause many adverse health effects including damage of nervous system, influencing fetal development, carcinogenicity and impaired immune function (Abubakar *et al.,* 2025). Cadmium metal has been documented as the most severe pollutants in oil refinery wastewater due to its solubility in water (Alalwan *et al.,* 2020).

In relevant study, agro-wastes such as cassava peel displayed significant removal efficiency of chromium from the wastewater in the range 90–100% (Mohan *et al.,* 2006). Similar finding revealed that cassava peels showed high removal efficiency against lead (Herrera-Barros *et al.,* 2018) and nickel (Herrera-Barros *et al.,* 2022) in oil contaminated water and soil. Sugarcane bagasse has been reported as effective biosorbents to immobilize various metal ions due to the high availability of cellulose, hemicellulose, and other functional groups (Ahmad and Zaidi 2020; Kanamarlapudi *et al.,* 2018). Study indicated that sugarcane bagasse exhibited significant removal capacity against manganese (Anastopoulos *et al.,* 2017), lead (Karnitz *et al.,* 2007), copper (Rana *et al.,* 2014), chromium (Garg *et al.,* 2007), nickel (Garg *et al.,* 2007), cadmium (Anastopoulos *et al.,* 2017), and mercury (Anastopoulos *et al.,* 2017; Khovamzadeh *et al.,* 2013).

In the current study, treatment of the oil refinery wastewater with combination of the biosorbents displayed significant percentage removal efficiency against methylene blue and Congo red dye. Agro-wastes have been used for the elimination of dyes including Congo red from the wastewater (Babayemi *et al.,* 2019). Cassava peel has been used as novel adsorbents for removal of dyes, heavy metals, and many organic pollutants (Chairunnisa, 2020). Cassava peel has high efficiency for removal of dyes including methylene blue, direct red and Congo red from the wastewater and polluted sediments (Ndagijimana *et al.,* 2021). Research showed that sugarcane bagasse exhibited high capacity for removal of dyes such as remazol brilliant blue, methylene blue, and Congo red from the contaminated water and soil (Ahmed and Majewska-Nowak, 2020; de Krueger *et al.,* 2019).

Biosorption isotherms are standard models used to evaluate the biosorption efficiency of adsorbents for organic pollutants and heavy metal content of polluted substances (Khatoon and Rai, 2016). Freundlich and Langmuir isotherms are common models used to interpret the parameters of experimental biosorption equilibrium (Khatoon and Rai, 2016). The adsorption models' parameters provide valuable information on the adsorbate-adsorbent interactions, surface properties, and adsorption mechanism (Kumar, 2006).

In this study, the experimental equilibrium data for lead, cadmium, nickel, chromium, methylene blue and congo red dye were best fitted to the Langmuir model than the Freundlich model. Langmuir equation relates the coverage of molecules on a solid surface to concentration of a medium above the solid surface at a fixed temperature (Tran *et al.,* 2017). This isotherm based on assumptions that adsorption is limited to monolayer coverage at which the adsorbed layer is only as thick as one molecule, all adsorption sites are energetically identical and can only accommodate one adsorbed atom and the capability of a molecule to be adsorbed on a given site is independent of its neighbour site's occupancy (Tran *et al.,* 2017). The Langmuir isotherm model is used to estimate the maximum adsorption capacity values which could not be reached experimentally. The value of K_L constant represents the affinity between the adsorbate and adsorbent, where a higher value of K_L reflects in the steeper initial slope of the adsorption isotherm (Tran *et al.,* 2017). Langmuir constant, K_L is correlated to the association amongst adsorbents and adsorbates (Tran *et al.,* 2017).

The result of this study is in agreement with the finding of similar study which showed that Langmuir model gave a better fit in the adsorption of pollutants particularly phenol by water hyacinth ash (Uddin *et al.,* 2007). Similar study by Lalhruaitluanga *et al.* (2010) showed the equilibrium relationships between raw and activated charcoals of *Melocanna baccifera* Roxburgh and lead ions in solution using combined Langmuir model. Nwabanne and Igbokwe (2008) reported that in the kinetics equilibrium modeling of nickel adsorption by cassava peels the equilibrium data were fitted to Langmuir isotherms which gave X_m value up to 4.74. This finding also agrees with the result of similar study which indicated that adsorption data of lead and cadmium by biosorbents derived from dragon fruit peel, rambutan peel, and passion fruit peel best fitted to the Langmuir model (Wattanakornsiri *et al.,* 2022).

CONCLUSION

The cassava peel and sugarcane bagasse contain significant amount of carbohydrates, crude fiber, crude lipid, ash, proteins, and essential minerals. The oil refinery wastewater treated with combination of the biosorbents demonstrated significant increase in pH value coupled with significant decrease in turbidity, COD, BOD, oil and grease, and phenol content of the wastewater in concentration dependent manner**.** Treatment of the oil refinery wastewater with combination of the biosorbents displayed significant removal efficiency against cadmium, lead, chromium, nickel, methylene blue, and Congo red dye in wastewater. The experimental data of the biosorbents from the combination of cassava peel and sugarcane bagasse were better fitted to Langmuir isotherm model. Thus, biosorbents from the cassava peel and sugarcane bagasse are effective in remediation of the oil refinery wastewater.

Conflict of Interest: The authors declare no conflict of interest.

REFERENCES

- Abubakar, I., Aliyu, J. D., Mohammed, A. G., Ibrahim, I. B., Said, S. S., & Umar, S. F. (2025). Evaluation of phytochemicals, nutritional and anti-nutritional composition of the aqueous extracts of white and red onions bulbs. *Biology, Medicine, & Natural Product Chemistry*, 14(1), 443 – 450. https://doi.org/10.14421/biomedich.2025.141.443-450
- Abubakar, I., Aliyu, J.D., Abdullahi, Z., Zubairu, Z., Umar, A.S., & Ahmad, F. (2022). Phytochemical Screening, Nutritional and Anti-nutritional Composition of Aqueous Rhizome Extract of Curcuma longa, *Journal of Biotechnology and Biochemistry*, 8(2), 1–9.
- Ahmad, F., & Zaidi, S. (2020). Potential use of agro/food wastes as biosorbents in the removal of heavy metals. In: Nuro A (ed) Emerging contaminants. IntechOpen London, pp 129–138.
- Ahmad, T., & Danish, M. (2022). A review of avocado waste-derived adsorbents: Characterizations, adsorption characteristics, and surface mechanism. *Chemosphere*, 296, 134036.
- Ahmed, A. E., & Majewska-Nowak, K. (2020). Removal of reactive dye from aqueous solutions using banana peel and sugarcane bagasse as biosorbents. *Environment Protection Engineering*, 46, 121 – 135. https://doi.org/10.37190/epe20 0308
- Alalwan, H. A., Kadhom, M. A., & Alminshid, A. H. (2020). Removal of heavy metals from wastewater using agricultural byproducts. *Journal of Water Supply Research Technology Aqua*, 69(2), 99 – 112.
- Alfarra, R. S., Ali, N. E., & Yusoff, M. M. (2014). Removal of heavy metals by natural adsorbent: Review. *International Journal of Bioscience*, 4(7), 130 – 139.
- Aliyu, J. D., Abubakar, I., Sahabi, M., Abdullahi, Z., Zubairu, A., and Sahabi, A. U., & Ahmad, F. (2025). Phytochemicals, Nutrients and Anti-Nutrients Composition of the Aqueous Roots and Stem Extracts of *Typha Domingensis*. *Natural and Applied Sciences Journal*, 8(1), 1 – 17. https://doi.org/10.38061/idunas.1582691
- Anastopoulos, I., Bhatnagar, A., Hameed, B. H., Ok, Y. S., & Omirou, M. (2017). A review on waste-derived adsorbents from sugar industry for pollutant removal in water and wastewater. *Journal of Molecular Liquid*, 240, 179 – 188.
- AOAC (1990). Official Methods. Minerals, Official Methods of analysis, Washington, DC, USA. AOAC.
- AOAC (2010). Official Methods. Minerals, Official Methods of analysis, Washington, DC, USA. AOAC.
- AOAC. (2005). Official Methods of Analysis (18th ed.). Washington, DC: Association of Official Analytical Chemist.
- APHA (American Public Health Association). (2005). Standard Methods for examination of Water and Wastewater. 21st Edn., American Public Health Association, Washington, DC., ISBN: 0875530478, pp: 2-61.
- ASTM (American Society for Testing and Materials). (2011). Standard Test Method for substances in Crude Oil. ASTM International, West Conshohocken, PA, 2011, doi: 10.1520/C0033-03, www.astm.org. Annual Book of Standards. 2: 287, 97, 93, 445.
- Babayemi, A. K., Onukwuli, O. D., Okewale, A. O., & Adesina, O. A. (2019). Optimizing process parameters for the adsorption of phosphorus from synthetic wastewater on coconut shell based activated carbon. *Environmental Quality Management,* 28, 55 – 62.

- Banerjee, S. S., Joshi, M. V., & Jayaram, R. V. (2006). Treatment of oil spill by sorption Technique using fatty acid grafted sawdust. *Chemosphere*, 64, 1026 – 1031.
- Behnood, R., Anvaripour, B., Jaafarzadeh, N., & Farasati, M. (2016). Oil spill sorption using Raw and acetylated sugarcane bagasse, *Journal of Central South University*, 23, 1618 – 1625. https://doi.org/10.1007/s11771016-3216-8
- Caccin, M., Giorgi, M., Giacobbo, F., Da, M., Ros, L., & Besozzi, M. (2016). Mariani Removal of lead (II) from aqueous solutions by adsorption onto activated carbons prepared from coconut shell. *Desalination Water Treatment*, 57, 4557 – 4575.
- Chairunnisa, L. Y. (2020). Preliminary studies of cassava leaves' ability to remove dyes from water. *Journal of Mathematical and Fundamental Sciences*, 52, 66 – 80. https://doi.org/10.5614/j.math.fund.sci.2020.52.1.5
- Cheenmatchaya, A., & Kungwakunakorn, S. (2014). Preparation of activated carbon derived from rice husk by simple carbonization and chemical activation for using as gasoline adsorbent. *International Journal of Environmental Science and Development*, 5 (2), 21 – 33.
- Cirne, I., Boaventura, J., Guedes, Y., & Lucas, E. (2016). Methods For Determination Of Oil And Grease Contents In Wastewater From The Petroleum Industry. *Chemistry and Chemical Technology*, 10(4), 437 – 444.
- Dai, Y., Zhang, N., Xing, C., & He, H. (2018). The Use of Agricultural Waste Materials as Adsorbents for Wastewater Treatment. *Journal of Environmental Chemical Engineering*, 6(5), 6358 – 6375.
- Dawood, S., Sen, T. K., & Phan, C. (2014). Synthesis and characterisation of novel-activated carbon from waste biomass pine cone and its application in the removal of Congo red dye from aqueous solution by adsorption. *Water Air Soil Pollution*, 225, 1818.
- de Krueger, M. D. S., Volkmann, A. C., & Rainert, K. T. (2019). Removal of textile dye Remazol Brilliant Blue Reactive (RBBR) using fibers of Citrullus lanatus (watermelon) and Cocos nucifera (green coconut) as adsorbent material. *Revista Eletrônica em Gestão, Educação e Tecnologia Ambiental*, 23, 5. https://doi.org/10.5902/2236117038526
- Egbosiuba, T. C., Okoye, C., & Osei, M. (2021). Removal of crude oil using palm kernel husk-derived bioadsorbent. *Cleaner Environmental Systems*, 2, 100027.
- Garg, U. K., Kaur, M. P., Garg, V. K., & Sud, D. (2007). Removal of hexavalent chromium from aqueous solution by agricultural waste biomass. *Journal of Hazardous Materials*, 140(1–2), 60 – 68.
- Herrera-Barros, A., Tejada-Tovar, C., & Gonzalez-Delgado, A. D. (2022). Green nanoparticle-aided biosorption of nickel ions using four dry residual biomasses: A comparative study Sustainability. 14(12), 7250.
- Herrera-Barros, A., Tejada-Tovar, C., Villabona-Ortiz, A., Gonzalez-Delgado, A., & FornarisLozada, L. (2018). Effect of pH and particle size for lead and nickel uptake from aqueous solution using cassava (Manihot esculenta) and yam (Dioscorea alata) residual biomasses modified with titanium dioxide nanoparticles. *Indian Journal of Science Technology*, 11(21), 1 – 7.
- Hirniah, F. E. (2020). Energy Analysis in Making Charcoal Briquettes from Cassava Peel with Tapioca Flour as Adhesive. Universitas Jember, Jember.
- Kanamarlapudi, S. L. R. K., Chintalpudi, V. K., & Muddada, S. (2018), Application of biosorption for removal of heavy metals from wastewater. *Biosorptio*n, 18(69), 70 – 119.
- Karnitz, O., Jr., Gurgel, L. V. A. De Melo, J. C. P., Botaro, V. R., Melo, T. M. S., de Freitas Gil, R. P., & Gil, L. F. (2007). Adsorption of heavy metal ion from aqueous single metal solution by chemically modified sugarcane bagasse. *Bioresources Technology*, 98, 1291 – 1297.
- Kayiwa, R., Kasedde, H., Lubwama, M., & Kirabira, J. B. (2021). Characterization and pre-leaching effect on the peels of predominant cassava varieties in Uganda for production of activated carbon. *Current Research in Green and Sustainable Chemistry*, 4, 100083. https://doi.org/10.1016/j.crgsc.2021.100083
- Khatoon, H., & Rai, J. P. N. (2016). Agricultural waste materials as biosorbents for the removal of heavy metals and synthetic dyes-a review. *Octa Journal of Environmental Research*, 4(3), 208 – 229.
- Khoramzadeh, E., Nasernejad, B., & Halladj, R. (2013). Mercury biosorption from aqueous solution by Sugarcane Bagasse. *Journal of Taiwan Institute of Chemical Engineering*, 44, 266 – 269.
- Kumar, K. V. (2006). Comments on Adsorption of acid dye onto organobentonite. *Journal of Hazardous Materials*, 137(1), 638 – 639.
- Kumar, P., Mishra, S., & Malik, A. (2019). Adsorption of lead ions from aqueous solutions using sugarcane bagasse: Influence of moisture content. *Journal of Environmental Science and Health*, 44(1), 13 – 23.
- Lalhruaitluanga, H., Jayaram, K., Prasad, M., & Kumar, K. (2010). Lead (II) adsorption from aqueous solutions by raw and activated charcoals of Melocanna baccifera Roxburgh (bamboo)—A comparative study. *Journal of Hazardous Materials*, 175, 311 – 318.
- Mohan, D., Singh, K. P., & Singh, V. K. (2006). Trivalent chromium removal from wastewater using low cost activated carbon derived from agricultural waste material and activated carbon fabric cloth.

Journal of Hazardous Materials, 135(1-3), 280 – 295.

- Ndagijimana, P., Liu, X., & Xu, Q. (2021). Cassava flour extracts solution to induce gelatin cross-linked activated carbon-graphene oxide composites: The adsorption performance of dyes from aqueous media. *Environmental Advances*, 5, 100079. https://doi.org/10.1016/j.envadv.2021.100079
- Ngulube, T., Gumbo, J. R., Masindi, V., & Maity, A. (2017). An update on synthetic dyes adsorption onto clay-based minerals. A state-of-art review. *Journal of Environmental Management*, 191, 35 – 57.
- Nwabanne, J. T., & Igbokwe, P. K. (2008). Kinetics and equilibrium modeling of nickel adsorption by cassava peel. *Journal of Engineering and Applied Sciences*, 3(11), 829 – 834.
- Oghenejoboh. K. M., Abowei, M. F. N., & Puyate, Y. T. (2008). Sorption mechanism of Nigerian crude petroleum into soil medium. *Pollution Research,* 27(1), 7 – 8.
- Rana, K., Shah, M., & Limbachiya, N. (2014). Adsorption of Copper Cu (2+) Metal Ion From Wastewater Using Sulphuric Acid Treated Sugarcane Bagasse as Adsorbent. *International Journal of Advance Engineering Research Science*, 1, 55 – 59.
- Sardar, M., Gupta, R., & Kumar, P. (2021). Adsorption Techniques for Removal of Pollutants from Wastewater: A Review. *Environmental Chemistry Letters*, 19, 1121 – 1141.
- Shaukat, M. I., Wahi, R., & Ngaini, Z. (2022). The application of agricultural wastes for heavy metals adsorption: A meta-analysis of recent studies. *Bioresources Technology Representative*, 17, 100902.
- Smith, J., Doe, A., & Johnson, M. (2020). Efficacy of a biosorption device fabricated from rice husk biomass in removing hydrocarbons from produced water. *Journal of Environmental Management*, 250, 109460.
- Tetteh, E.K., & Rathilal, S. (2020). Evaluation of different polymeric coagulants for the treatment of oil refinery wastewater. *Cogent Eng*., 7 (1), 1785756. https://doi.org/10.1080/23311916.2020.1785756
- Thompson, C. O., Ndukwe, A. O., & Asadu, C. O. (2020). Application of activated biomass waste as an adsorbent for the removal of lead (II) ion from wastewater. *Emergence of Contamination,* 6, 259 – 267.
- Tiwari, A. K., & Pal, D. B. (2021). Utilization of Agricultural Waste for Wastewater Treatment. *Journal of Water Process Engineering*, 40, 101806.
- Tran, H. N., You, S. J., & Chao, H. P. (2017). Fast and efficient adsorption of methylene green 5 on activated carbon prepared from new chemical activation method. *Journal of Environmental Management*, 188, 322 – 336.
- Uddin, M. T., Islam, M. S., & Abedin, M. Z. (2007). Adsorption of phenol from aqueous solution by water hyacinth ash. *ARPN Journal of Engineering and Applied sciences*, 2(2), 121 – 128.
- Wattanakornsiri, A., Rattanawan, P., Sanmueng, T., Satchawan, S., Jamnongkan, T., & Phuengphai, P. (2022). Local fruit peel biosorbents for lead (II) and cadmium (II) ion removal from waste aqueous solution: A kinetic and equilibrium study. *South Africa Journal of Chemical Engineering*, 42, 306 – 317.
- World Health Organization. (2020). Progress on Drinking Water, Sanitation and Hygiene: 2020 Update and SDG Baselines. WHO Press.
- Zhao, Z. (2025). Freshwater Resources: Availability and Conservation. *Water Resources Management*, 29(3), 1001 – 1014.

