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Remediation of Colour from distillery wastewater using orange peels as adsorbent

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ABSTRACT

The dark-brown colour of Distillery Wastewater (DWW), often termed melanoidin, causes discolouration and turbidity rise in water bodies, restraining water usage and detrimental to aquatic life. This study investigates Orange Peels (OP) efficiency as a low-cost adsorbent for color removal from DWW. The colour of Fresh DWW's was confirmed on a platinum-cobalt colour scale, its colour concentration was measured at 620 nm using a UV-visible spectrophotometer. OP was carbonized and characterized for chemical composition, specific surface area, surface functional group and surface morphology. Batch adsorption experiment was performed on Orange Peel Carbon (OPC) and compared with coal-based commercial activated carbon (ACC) to determine the effects of agitation speed, retention time, carbon dosage, DWW pH on the Maximum Removal Efficiency (MRE) of colour. The adsorption capacity was evaluated using Langmuir, Freundlich, Elovich, Pseudo-first-order and Pseudo-second-order models. OPC showed good-quality adsorbent. DWW was dark-brown in color (2.030 Abs). A 60.20 % MRE was achieved at 100 RPM agitation speed, 60 mins retention time, 2.5 g/100ml OPC dosage and pH of 4.0. ACC showed better performance of 79.46 % color removal. The adsorption followed Elovich isotherm, implying multilayer adsorption with a correlation factor of 0.9414. In general, OPC proved effective in reducing colour from DWW, and thus, recommended as a suitable adsorbent to replace the costly commercial adsorbents for DWW treatment.

INTRODUCTION

Distilleries generate mickle volume of wastewater from processing activities, with an average volume of 8 to 15 litres released during production of one litre of alcohol (Chowdhary *et al*., 2018). Generally, DWW is classified as high-strength industrial wastewater and environmentally tagged 'RED' due to its high content of lowly degradable organic matter (Arimi *et al.*, 2014). DWW is characterized by brown or dark colour, loathsome smell, elevated temperature, acidic pH, total soluble solids, high biochemical/chemical oxygen demand, heavy metals, various salt contents and other organics (Jain and Srivastava, 2012a). Its disposal into the environs before sufficient treatment causes serious environmental dangers, deteriorating the qualities of soil, water, and in due course, groundwater, a matter of concern for both aesthetical and eco-toxicological reasons. The dark-brown colour of DWW, often termed melanoidin, causes discolouration and turbidity rise in the water body, increasing the degree of sedimentation and reducing sunlight penetration, photosynthetic activity and dissolved oxygen concentration in the water body. These activities restrain the usage of water and choke off animals and plants (Narain *et al*., 2012), making life unbearable and sometimes detrimental to the aquatic life forms, reducing the edible ones – a source of

protein and other nutrients needed by humans for survival. Therefore, sufficient treatment of DWW up to the standard level before being channelled into the environment is indispensable.

Among the treatment methods adopted so far, the process of adsorption (a physicochemical treatment technology), using activated carbon as an adsorbent, has been the most substantiated method (Ojoawo *et al*., 2022; Olaoye *et al*., 2021). Yet, it is unfortunate that the needed adsorbent (activated carbon) for this process is highly expensive (Ojoawo *et al*., 2022; Olaoye *et al.* 2018), most especially in Nigeria and similar developing countries that had to import them, thus, ascertaining low-cost activated carbon with comparative efficacy has been the research concentration in recent years (Ojoawo *et al*., 2022). Synthesizing activated carbon from agricultural and agro-industrial wastes for the adsorption processes is at present and in general receiving all-embracing attention due to their possessive features such as high adsorption capacity (outstanding pollutant-binding capacity, efficiency and lifelike at removing pollutants), copious availability, no or low cost, easy-to-make chemical modification, less disposal problem after adsorption and easy regeneration (Aremu *et al*., 2020, Olowonyo *et al*, 2023, Bhatnagar *et al*., 2015).

Research has shown that waste generated from consumption of orange fruit was between 30 to 35 % (Rafiq *et al.,* 2018), with its global processing generating approximately 32 million tons of peels per year (Michael-Igolima *et al*., 2023). These peels are discarded and sent to garbage as under-utilized materials, which further create a nuisance to the community, environmental aesthetics and biodiversity. The orange peels, containing around 80 % water, rot quickly, invite microbes, flies and mould, and also produce mycotoxins (Suri *et al*., 2022). These activities induce a high number of toxic compounds into the environment and further deteriorate soil and water quality, and in due course, groundwater (Suri *et al*., 2022). It is, therefore significant and essential to find applications or usage for these peels. In addition, orange peels have been reported to have components and important functional groups, such as pectin, hydroxyl, carbonyl, hydroxyl, carboxyl and amine groups, found in other agricultural wastes (such as banana peels, coconut shell and maize corn cobs) with high adsorption capacity (Bhatnagar *et al*., 2015).

Investigations revealed that treatment of wastewater colour is important before it is discharged into a water body (Arimi *et al*., 2014) and OP currently constitutes a solid residue that has not been adequately applied despite the large quantity of its generation worldwide (Akinhanmi *et al*., 2020). In this view, this study was conducted to investigate the removal of colour from distillery wastewater using orange peels as a cost-effective adsorbent. Its usage will not only serve as a means of DWW decontamination but will also add value to its initial perceptions as agricultural waste. Rather, the peels will be recovered, recycled and preserved for monetary value thereby freeing the environment from potential toxicology that could arise from its indiscriminate disposal.

MATERIALS AND METHOD

Collection of Samples

Freshly OP was sourced from the orange sellers in Ile-Epo market, Alimosho local government area of Lagos State, Nigeria (6.6393^{o}N, 3.2962^{o}E). Fresh sample of DWW was obtained from an Indigenous Distiller Company in South Western Nigeria. The temperature of the DWW was measured and kept at 4 ^{o}C until used. A coal-based commercial activated carbon (Calgon US activated carbon) was procured from I-Resources Global, Isolo, Lagos State, Nigeria (6.5225^{o}N, 3.3351^{o}E). Distilled water, high-purity analytical reagents and chemicals were

obtained from the Federal Institute of Industrial Research, Oshodi, analytical laboratory (FIIRO-ANALAB), Lagos state, Nigeria (6.5477ºN, 3.3553ºE). The reagents are used without further purification.

Preparation of Orange Peel Adsorbent

Orange peels were thoroughly washed, air dried under ambient temperature for 2 hrs., dried in a hot air oven at a temperature of 80 ± 2 ºC for 12 hrs. (Akinhanmi *et al.*, 2020) and pulverized in a laboratory grinder. The powder was sifted through 0.5 mm sieve and carbonized in the laboratory electric muffle furnace for 2 hrs. at 250 ± 5 ºC. The carbonized OP was allowed to cool to room temperature and then washed with distilled water to a neutral pH. The Orange peel adsorbent was kept in a desiccator for further use.

Characterizations of Orange Peel Carbons

Orange Peel Carbon (OPC) and coal-based Commercial Activated Carbon (AC_C) were characterized using proximate analysis for ash contents, fixed carbon, moisture and volatile matter content of the carbon samples were determined respectively by loss on drying process, heating process under an inert atmosphere, estimation and direct combustion (ASTM WK84623, 2022). The Brunauer–Emmett–Teller (BET) analysis was performed with the aid of Quanta Chrome Instrument to obtain the BET surface area, pore volumes and pore diameter as described by Sneha *et al*., (2022). The surface functional properties were studied using Fourier Transform Infrared Spectroscopy (FTIR) using standard ASTM techniques (ASTM E168, 2016). While, the surface morphology images were observed by Scanning Electron Microscope (SEM) on Zeiss EVO50 (Oberkochen, Germany) at 15 kV and a magnification of 1000x using standard ASTM techniques (ASTM E986, 2016) with suitable matching.

Characterization of Distillery Wastewater

The physical colour of the obtained distillery wastewater was confirmed on a platinum-cobalt colour scale, while, the colour concentration was measured at a maximum wavelength of 620 using a UV-visible spectrophotometer (ASTM D1209, 2022).

Adsorption Experiments: Treatment of Distillery Wastewater

Batch adsorption experiments at room temperature (27 – 30 ºC) were carried out to define the optimum agitation speed, retention time, carbon dosage and solution pH for effective removal of colour from distillery wastewater. Fresh distillery wastewater was first kept at pH 7.0 (adjusted as necessary by adding 0.1N HCl or 0.1N NaOH solution). The adsorption factors considered were agitation speed (50, 100, 150, 200 and 250 rpm), retention time (20, 40, 60, 80 and 100 minutes), adsorbent dosage (0.5, 1.0, 1.5, 2.0 and 2.5 grams) and solution pH of 2.0, 4.0, 6.0, 8.0, and 10.0.

One (1) g of each carbon sample is put into 100ml of distillery wastewater, agitated in a rotary mechanical shaker at the variant agitation speed for 60 minutes, kept under undisturbed condition for one hour (1 hr.) for settlement and then filtered through 0.45 µm filter paper (Whatman). The filtrates were then analyzed for colour and compared with the initial value to determine the removal's optimum agitation speed (Ojoawo *et al.*, 2022). A sample with no carbon sample served as a control. The same procedure was followed to determine the removal optimum retention time, carbon dosage and solution pH using the variant retention time, carbon dosage, and solution pH, keeping onto the optimums respectively. The adsorption capacity – Qe (mg/g) and removal efficiency – R_e (%) were calculated using eqn. 1 and 2, respectively:

Adsorption capacity (Q_e) $= \frac{(Co-Ce)\,V}{M}$ (1)

Percentage removal (R_e) $= \frac{(Co-Ce)\,100}{Co}$ (2)

where 'v' is the distillery wastewater volume (mL), Co is the adsorbate's initial concentration before the processes of adsorption (mg/L), Ce is the final concentration of the adsorbates after the processes of adsorption (mg/L), M is the weight in gram of the carbon sample.

Adsorption Isotherm Studies and Models

To investigate the equilibrium conduct of the carbon samples, Langmuir, Freund-lich and Elovich isotherms were adopted and expressed by equations (3 & 4), (5) and (6) respectively (Ayawei *et al.*, 2017)

Langmuir Isotherm: $\frac{Ce}{Qe} = \frac{1}{Q\text{m}}.\frac{1}{Kl} + \frac{Ce}{Q\text{m}}$ (3)

where Q_e is the adsorbed concentration at equilibrium (mg/g), Q_m is the maximum uptake at equilibrium (mg/g), C_e is the concentration at equilibrium (mg/L) and K_L is Langmuir isotherm constant. The Langmuir constants q_m and K_L are calculated from the slope and intercept of the plot between $1/Q_e$ versus $1/C_e$. To discover the adsorption process efficiency, separation factor (R_L) was calculated by equation (4):

$R_L = \frac{1}{1+KL\,Ce}$ (4)

Freundlich Isotherm:

$\text{Log Qe} = \text{Log Kf} + \frac{1}{nf}\,Log\,Ce$ (5)

where K_f and n_f are well-defined as the constants for the adsorption capacity and adsorption intensity respectively. The plot of Log q_e versus Log C_e gives the slope $1/n_f$ and intercept K_f {(mg/g) / (L/g)}. K_f is the Freundlich constant related to the carbon's adsorption intensity (mg/g) and n_f is the Freundlich exponent.

Elovich Isotherm: $ln\frac{Qe}{Ce} = \ln(K_E Q_m) - \frac{Qe}{Qm}$ (6)

Where Qm is the Elovich maximum adsorption capacity (mg/g) and K_E is the Elovich equilibrium constant (L/mg). K_E and Qm are respectively known from the intercept and slope of the straight line of ln (Qe/Ce) vs. Qe.

Adsorption Kinetic Studies and Models

Pseudo-first and -second order models were adopted to simulate the distillery wastewater adsorption kinetics onto the carbon samples. The models are generally displayed in linear form as shown in equation (7) and (8):

Pseudo-first-order kinetic model:

$\text{Log}\,(q_e - q_t) = \text{Log}\,(q_e) - \frac{K1}{2.303}\,t$ (7)

Pseudo-second order kinetic model:

$\frac{t}{q_t} = \frac{1}{K_2(q_e)(q_e)} + t\frac{1}{qe}$ (8)

Where, K_1 and K_2 are the adsorption rate constants of pseudo-first and - second order kinetic model respectively, q_t is the adsorbed contaminants quantity at a specific time 't' (minute), q_e is the adsorbed contaminants quantity at equilibrium. A plot "log (q_e - q_t)" versus "t" gives a straight line from which K_1 and q_e can be calculated from the slope and intercept. A plot "t/q_t" versus "t" gives a straight line from which K_2 and q_e can be evaluated from the slope and the intercept of the plot of the second-order kinetic equation is valid.

Statistical Analysis

The experiments were carried through in triplicate and average values with standard errors were reported. The statistical significance of the observed differences among means of triplicate reading of the experimental results was determined by variance analysis (SPSS software version 23.0 computer package) while means were separated using

Duncan's Multiple Range Test (DMRT) at 5% significance level ($P < 0.05$), and Least Significant Difference (LSD) to establish any significant differences amongst the samples. Results were presented as mean ± standard deviation from the mean. Parameters of isotherms and kinetics were calculated by non-linear regression using the calculation of the least squares method. The curve fitting and statistical analysis were performed using SPSS software. The correlation coefficient (R^2) and standard error (SE) of the estimates obtained from regression were employed to compare the model's applicability (Weaver *et al.*, 2017).

RESULTS AND DISCUSSION

Characteristics of OPC and ACc

The proximate, ultimate and porosity characteristics of orange peel carbon (OPC) in comparison to a coal-based Commercial Activated carbon (AC_C) are shown in Table 1. OPC holds ash (4.08%), fixed carbon (52.41%), moisture (7.10%) and volatile matter (36.41%) in the recommended range for a good-quality carbon adsorbent (Table 1). In comparison, OPC retains the highest moisture and volatile matter as well as the lowest ash and fixed carbon contents, while, AC_C possesses the opposite. The Brunauer–Emmett–Teller (BET) analysis revealed OPC with a surface area (1240.65 m^2g^{-1}) that facilitates excellent adsorption having found in the range of between 450 and 2,000 $m^2g{-}1$ (Sneha *et al*., 2022), total pore volume of 0.404 cm^3g^{-1} and average pore diameter of 32.535 A. Yet, AC_C holds better attributes.

Figure 1 shows the spectra results of FTIR spectroscopy analysis conducted to identify some main characteristic functional groups in OPC as compared to AC_C. The carbon-oxygen functional groups that are present on the surface of carbon-based adsorbent are one of the most critical characteristics that control and determine the carbon's adsorption (Zhuang *et al*., 2020). As shown, the carbons display strong adsorption peaks in the region of 4000 – 350 cm^{-1}. In the two spectra, a wide-ranging band was observed between 3868 - 3210 cm^{-1}, 2932 - 2120 cm^{-1}, 1997 - 1440 cm^{-1}, 1250 - 1025 cm^{-1}, 960 - 502 cm^{-1} and 451 - 373 cm^{-1}. Idiosyncratically, the functional groups with absorptive peaks between 3,868 and 3,210 cm^{-1} are identified as O-H antisymmetric stretching vibration of surface hydroxyl groups like cellulose, hemicellulose and lignin (Zhuang *et al*., 2020) while, the asymmetric stretching vibration peak observed between 2,932 and 2,120 cm^{-1} was assigned to aliphatic C–H in the CH_2 and CH_3 groups (Ngueabouo *et al.*, 2022). The peak around 1,997 and 1,440 cm^{-1} belongs to the non-symmetric vibration absorption of C=O in hemicellulose and lignin, and the vibration absorption of C=C aromatic compounds in benzene ring (Ngueabouo *et al.*, 2022). The absorption due to stretching vibrations of C–O bond in carboxylic acids, alcohols, phenols, ethers, and esters was typically positioned at 1250 cm^{-1} - 1025 cm^{-1} (Ofudje *et al.* 2017). The bands observed between 1,000 and 500 cm^{-1} are owing to the out-of-plane deformation mode of C-H for alkene aromatic rings, while, the intense band below 500 cm^{-1} was described as the vibration structure of inorganic molecules (Bohli *et al*., 2015). Notably, some absorption peaks were significantly reduced in the AC_C. The microphotographs showing the morphology of the carbons as characterized by Scanning Electron Microscope (SEM) are shown in Figure 2. As shown, the external morphology of OPC was relatively smooth and dense, only showing the tubular channels of the orange peel itself with observable minimal porous cavities (microstructure). AC_C appears coarser on the external surface than OPC and presents heterogeneous pores of various sizes and shapes which are the entryway into internal mesopores and micropores.

Table 1: Characteristics of OPC and Acc

Characteristics	OPC	AC_C	Recommended	Reference
Proximate Composition				
Ash content (%)	4.08 ± 0.030^{c}	6.97 ± 0.040^{a}	2 - 10 %	Mariana et al., 2021
Fixed carbon content (%)	52.41 ± 0.01^{c}	74.97 ± 0.30^{a}	50 - 90 %	Beksissa et al., 2020
Moisture content (%)	7.10 ± 0.030^{a}	5.88 ± 0.040^{b}	5 - 15 %	Mariana et al., 2021
Volatile matter content (%)	36.41 ± 0.50^{a}	12.18 ± 0.40^{c}	15 - 25 %	Hanum et al., 2017
BET Surface Area and Porosity				
Average pore diameter (A)	32.5350^{c}	40.6500^{a}	-	-
Total pore volume ($cm^3\ g^{-1}$)	0.40400^{d}	0.85700^{a}	-	-
Total surface area (m^2 g-1)	1240.65^{c}	1517.51^{a}	450 - 2,000	Sneha et al., 2022

Values are mean of 3 replicates ± standard deviation and the means within a row with the same letters are not significantly ($P \leq 0.05$) different.
OPC - non activated orange peels carbon; AC_C - commercial activated carbon

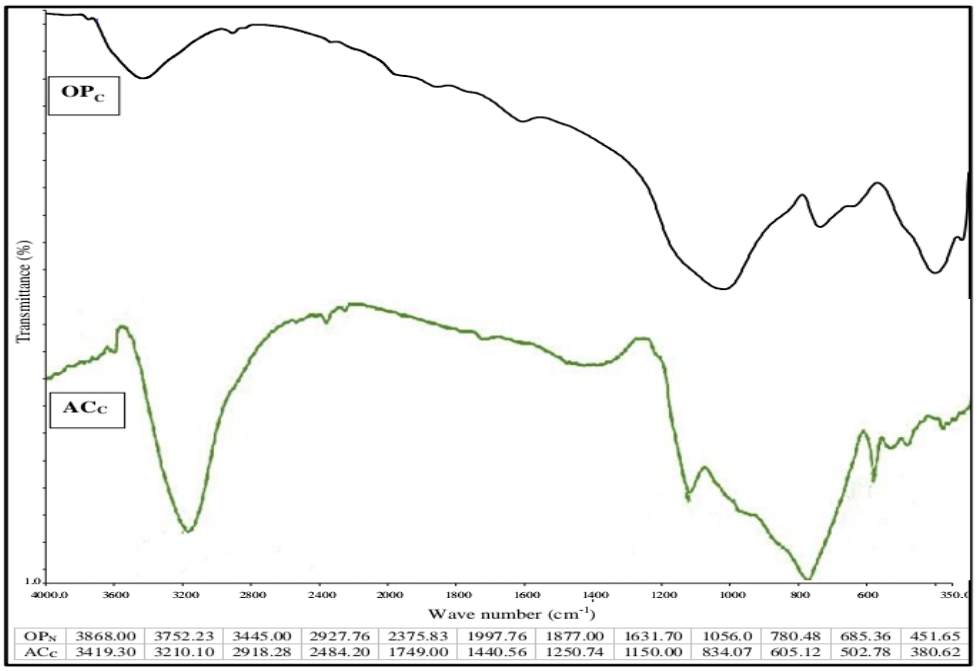

Figure 1: FTIR Absorption Spectra of Orange Peels Carbons and Acc

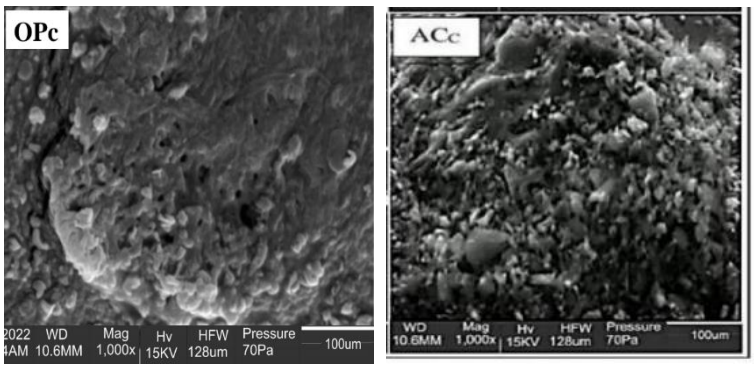

Figure 2: Scanning Electron Microphotographs (SEM) of Orange Peels Carbons and Acc

Carbons with microporous structures are projected for high adsorption capabilities owing to an offer of active sites (Michael-Igolima *et al.*, 2023). Generally, the OPC's characteristics suggest that they have great potential for good adsorbents and would be acceptable for any application involving adsorption.

Characteristics of Distillery Wastewater

Fresh distillery wastewater was noted with a dark-brown colour in addition to an initial concentration of 2.030 Abs. at a maximum wavelength of 620. The observed colour could be owing to the creation of caramelized sugar during alcohol processing (Terefe and Eyob, 2015), or as a result of Iron (Fe) and Manganese (Mn) presence in the water, the combination of these two metals causing dark-brown coloured solution through oxidation (Khadse *et al*., 2015). The initial colour concentration and the subsequent ones from the adsorption experiments were compared to define the percentage at which colour is reduced/removed from distillery wastewater. Colour is an overall determinant of water cleanliness and to remove it from wastewater and different classes of solution, the adsorption process using activated carbon has been evaluated extensively.

Adsorption Efficiency of OPC and Acc

The adsorption variations of colour from distillery wastewater onto orange peel carbon (OPC) and coal-based commercial activated carbon (AC_C) with agitation speed, retention time, carbon dosage and solution pH are shown respectively in Figure 3 while Table 3 showed the optimum values and maximum percentage removals of the adsorption studies.

Effect of Agitation Speed on the Adsorption Processes

The maximum adsorptions of colour onto OPC (48.47%) and ACc (59.60%) occurred at the same agitation speed of 100 RPM. It was experimental that the adsorption increases promptly with the first increase in agitation speed, but, then decreases. Attaining adsorption peak at 100 RPM could be explained by the fact that all the available active sites of the carbon and substantial colour concentration are maximum (all-out) at the same time, giving room for the driving forces of adsorption to be maximum (Ofudje *et al*. 2017). Further, a decrease in adsorption after the adsorption peak signals desorption - the release of the adsorbed colour from the carbon surface.

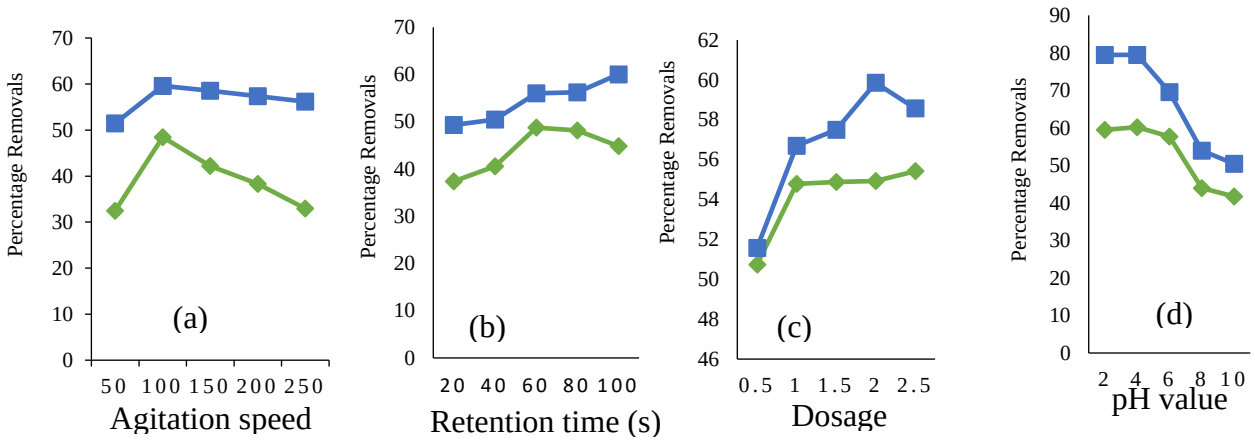

Fig 3. Effect of operating variables on removal efficiency: (a) agitation speed, (b) retention time, (c) dosage and (d) pH

Effect of Retention Time on the Adsorption Processes

The maximum adsorptions of colour onto OPC (48.76%) and AC_C (60.04%) occurred at retention times of 60 and 100 minutes respectively. Onto OPC, the adsorption efficiency increases from the first considered time up to 60 minutes and then declines, but onto AC_C, the adsorption increases with increasing retention time up to the last considered time. The instant adsorption of colour could be ascribed to the timely adsorption occurring on the outer surface of the carbons, followed by the delayed adsorption occurring inside the carbon pores. Immediately the maximum contaminant that a carbon can hold (in both outer and inner surface) is reached and no extra contaminant is attracted, the carbon gets saturated and the rate of adsorption tends to cease or reduce, so, what had been adsorbed gets released if time is increased further (Olaoye *et al*., 2020), like in the case of OPC usage.

Effect of Carbon Dosage on the Adsorption Processes

The maximum adsorption of 55.42% colour occurred on the usage of 2.5gm OPC, while, 59.85% maximum adsorption was achieved on the usage of 2.0 gm AC_C. The shared patterns of better adsorptions with an increase in carbon dosage are due to the presence of more available binding sites. The higher the quantity of carbon adsorbent, the greater the surface area and quantity of active sites for the adsorption of contaminants (Arica *et al.*, 2018). The observed decrease in colour adsorption onto AC_C, might be owing to the aggregation or congestion of superfluous carbon particles (Ojoawo *et al.*, 2022).

Table 3. Optimum Values and Maximum Percentage Removals of the Adsorption Studies

Variables	Optimum Values	Maximum % Removals
OPC		
Agitation Speed (RPM)	100	48.47
Retention Time (minutes)	60	48.76
OPC Dosage (gram)	2.5	55.42
Distillery Waster pH	4.0	60.20
AC_C		
Agitation Speed (RPM)	100	59.60
Retention Time (minutes)	100	60.04
AC_C Dosage (gram)	2.0	59.85
Distillery Waster pH	2.0	79.46

Effect of Changes in Distillery Wastewater pH on the Adsorption Processes

The maximum adsorptions of colour onto OPC (60.20%) and AC_C (79.46%) occurred at pH of 4.0 and 2.0 respectively. The removal of colour onto either of the carbons is higher in low-pH distillery wastewater (acidic) but lower in high pH (basic). This could be clarified by the fact that, under acidic conditions (pH 2 - 6), the carbon surface is highly protonated (becomes positively charged), (Chunfang *et al.*, 2017), which in turn, becomes attracted to the negatively charged ions of melanoidin (distillery wastewater colour). As the pH of distillery wastewater is increased to basic form (pH 8 - 14), the carbon surface becomes deprotonated (negatively charged owing to the highly concentrated hydroxide ions (OH^-) from the diluent - NaOH), (Ofudje *et al.*, 2017), compelling the colour adsorption to reduce drastically due to electrostatic force of repulsion.

The summary of the findings from the adsorption study is shown in Table 3. Generally, the concentration of colour in the distillery wastewater was reduced from 2.030 Abs to 0.808 and 0.417 Abs

using OPC and AC_C respectively, indicating that 60.20 and 79.46% maximum removal efficiency was achieved and at 100 RPM agitation speed, 60- and 100-mins retention time, 2.5 and 2.0/100ml carbon dosage and pH of 4.0 and 2.0 respectively. Though AC_C showed better performance, OPC proved effective in colour reduction from distillery wastewater and showed potential in replacing the costly commercial adsorbents for DWW treatment.

Adsorption Isotherms

The adsorption isotherms for process design and equilibrium behaviour of OPC and AC_C in remediating distillery colour is shown with the Langmuir, Freundlich and Elovich isotherms. The attained results with their respective plots are précised respectively in Figures 4, 5 and 6. Isotherm constants were calculated and the results were tabulated (Table 4). The 'R^2' values of correlation coefficients were used to assess the value of the isotherm equations. The separation factor (R_L) and slope (value of 1/n) were used to confirm whether the adsorption is linear (R_L or 1/n = 1), unfavourable (R_L or 1/n > 1), favourable (0 < R_L or 1/n < 1) or irreversible (R_L or 1/n ~ 0).

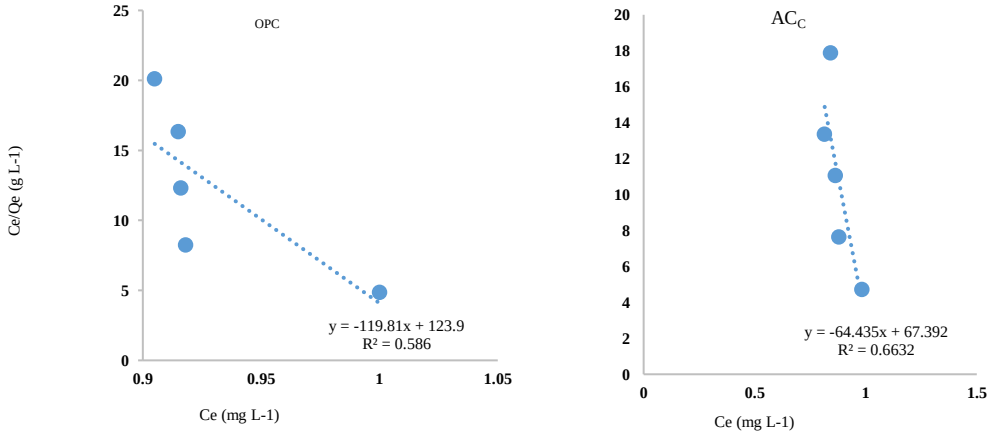

Figure 4: Langmuir Adsorption Isotherms of Color onto OPC and AC_C

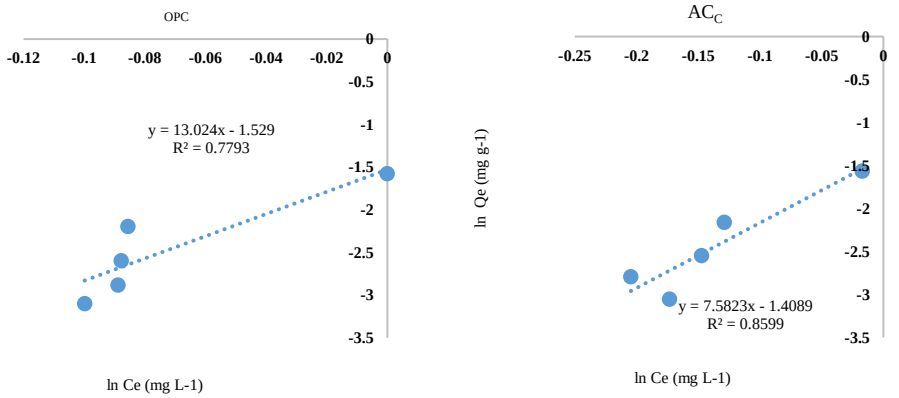

Figure 5: Freundlich Adsorption Isotherms of Color onto OPC and AC_C

Comparative Annotations on the Adsorption Isotherm Models

Adsorption phenomenon is better denoted by isotherm with a higher correlation coefficient (R^2) value (Ayawei *et al*., 2017). Correspondingly, the adsorption of colour onto OPC and AC_C was best described by Elovich isotherm model. Model with correlation coefficient (R^2) of 0.9414 and 0.9390 respectively. Fitting of data into Elovich isotherm model shoulders that the adsorption sites increase

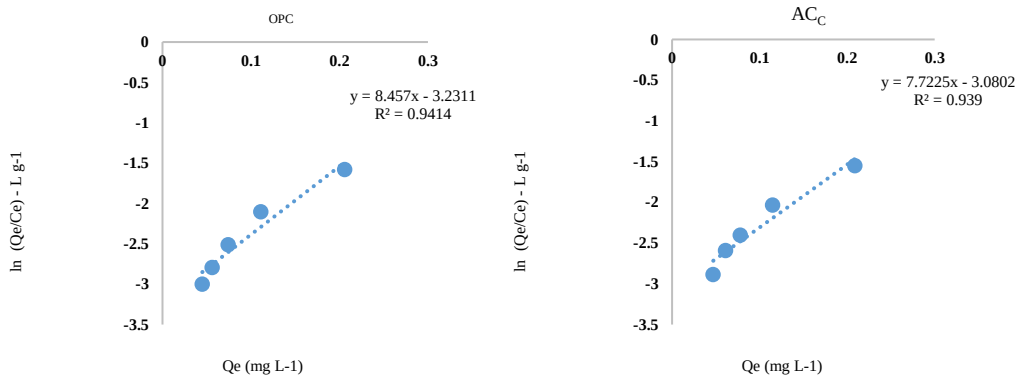

Figure 6: Elovich Adsorption Isotherms of Color onto OPC and AC_C

Table 4: Isotherm Model Constants for the Adsorption Studies

Parameters	Langmuir Isotherm				Freundlich Isotherm			Elovich Isotherm		
	Q_m (mg/g)	K_L (L/mg)	R_L	R^2	1/n (L/mg)	K_F (mg/g)	R^2	K_E (L/mg)	Q_m (mg/g)	R^2
OPC Color	0.0081	-1.0341	-0.9097	0.5860	13.024	0.0296	0.7793	-3.2311	8.4570	0.9414
AC_C Colour	0.0148	-1.0459	-0.8903	0.6632	7.5823	0.0390	0.8599	-3.0802	7.7225	0.9390

Keys: OPC - non activated orange peels carbon; AC_C - commercial activated carbon

exponentially with adsorption, multilayer adsorption took place and the adsorbing surface is heterogeneous (Ayawei *et al*., 2017). Correspondingly, the adsorption of colour onto OPC and AC_C was best described by Elovich isotherm model. Model with correlation coefficient (R^2) of 0.9414 and 0.9390 respectively. Fitting of data into Elovich isotherm model shoulders that the adsorption sites increase exponentially with adsorption, multilayer adsorption took place and the adsorbing surface is heterogeneous (Ayawei *et al*., 2017).

Adsorption Kinetic Model

Adsorption kinetic helps define the phenomenological coefficients that characterize the transport of adsorbates within an adsorbent (Bediako *et al*., 2016b). The adsorption rate of colour from distillery wastewater onto orange peel carbons (OPC) and AC_C was studied and the rate constants of the process were determined using pseudo-first-order and pseudo-second-order kinetic models. The models' plots were presented respectively in Figures 7 and 8, kinetic parameters were presented in Table 5 and the best fit of the kinetic models was established by means of the obtained data.

Comparing the correlation coefficient (R^2) values of the two models on the basis of which is higher, all the adsorption experimental data was replicated by second-order kinetic model with 'R^2' in all the cases close to one. Worth mentioning that if experimental data fits well with pseudo-second-order kinetic model, it indicates chemisorption controls the adsorption rate (Kumar *et al*, 2011), which involves a covalent bond between the adsorbate and the surface of the adsorbent.

Table 5: Kinetic Model Constants for the Adsorption Processes

Parameters	Pseudo-First Order Kinetic Model			Pseudo-Second Order Kinetic Model		
	K_1	**Qe**	**R^2**	**K_2**	**Qe**	**R^2**
OPC Colour	-0.0382	0.0033	0.5543	-17.580	0.0953	0.9697
AC_C Colour	-0.0440	0.0189	0.5045	0.9673	0.1289	0.9948

Keys: OPC - non-activated orange peels carbon; AC_C - commercial activated carbon

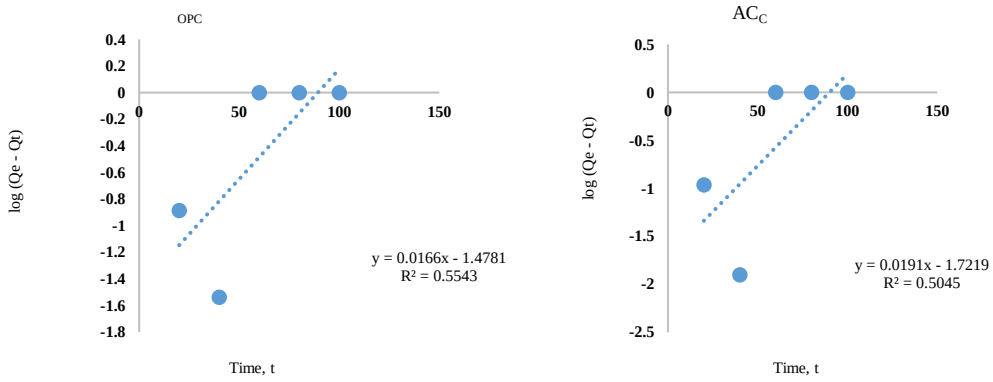

Figure 7: Pseudo-First Order Plot for the Adsorption of Color onto OPC and AC_C

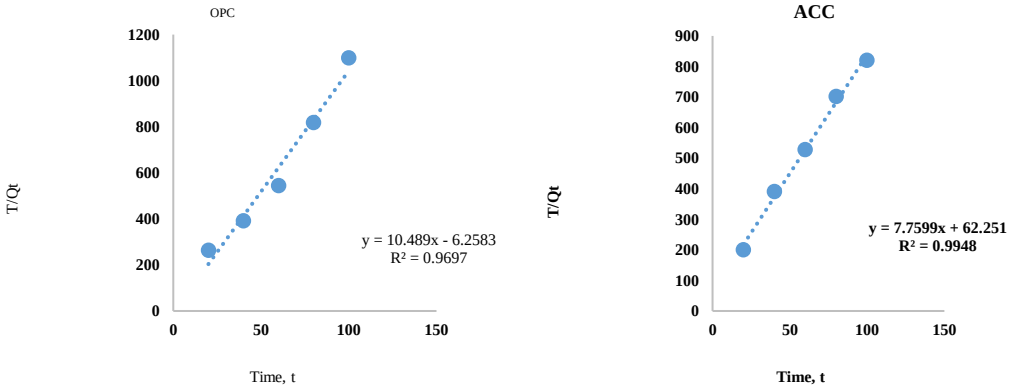

Figure 8: Pseudo-Second Order Plot for the Adsorption of Color onto OPC and AC_C

CONCLUSIONS

This study presents the feasibility of using orange peel carbon in remediating distillery wastewater colour. The characteristics of orange peel carbon (OPC) suggest that it has great potential as a good adsorbent and would be acceptable for any application involving adsorption. Fresh distillery wastewater was characterized by a dark-brown coluor (2.03 Abs). The adsorption study revealed that the concentration of colour in the distillery wastewater is reduced from 2.03 Abs to 0.808 and 0.417 Abs using OPC and AC_C respectively. A 60.20 % maximum removal efficiency was achieved at 100 RPM agitation speed, 60 mins retention time, 2.5g/100ml OPC dosage and pH of 4.0. AC_C showed better performance of 79.46 % colour removal. The colour's adsorption onto the two carbons followed Elovich isotherm and Pseudo-second-order kinetic models. Though AC_C provided the best adsorption capabilities, OPC provided an embracing removal of colour from distillery wastewater and can replace the costly commercial carbon adsorbent. This study assumed that if substantial quantities of recalcitrant colour (melanoidin) are adsorbed, there is a possibility that other distillery wastewater contaminants would as well have been adsorbed. However, the re-usability potential of OPC needs to be investigated.

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