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Biosorption of Colour, Copper and Zinc in Textile Wastewater using Carbonized Orange Peels

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Abstract

Recently, low-cost adsorbents from sustainable sources are required for the remediation of textile wastewater. Carbonized Orange Peels (COPs) was utilized in remediating colour, Zinc and Copper from textile wastewater. The initial and final pH, colour and trace metals' composition of the wastewater used were determined for the adsorption processes. Batch adsorption experiment was carried out on COPs and textile wastewater's mixture to find effects of COP's dosage, agitation, pH and contact time on the colour, Zinc and Copper's removal from the wastewater. The adsorption isotherms and kinetic studies were conducted using Langmuir, Freundlich, Pseudo-first-order and Pseudo-second-order models. Findings established that the optimum removal of colour, Zinc and Copper respectively occurred at an adsorbent dosage of 2.5, 0.5 and 3.0 g/100ml, pH of 10, 4 and 2, rotating speed of 100, 250 and 250 rpm, contact time of 40, 60, and 40 mins. The adsorption isotherms revealed only copper adsorption as optimum and well fitted Langmuir isotherm. Pseudo-second-order kinetic model best suited adsorption data of the colour and metal ions with high correlation coefficient (R^2) exceeding 0.95. Conclusively, COPs is effective in remediating the colour, copper and zinc from the wastewater, thus, recommended as suitable adsorbent for treatment of textile wastewater.

Keywords: Batch adsorption, Carbonized, Orange peel, Textile wastewater.

Introduction

Textile wastewater is a muddle of dyes, organic compounds, trace metals, total dissolved solids, grits, salts, surfactants, chlorinated compounds, chemical and biological oxygen demand; and in the colouring processes, the proportion of lost textile wastewater is fifty percentage of the dye owing to the insignificant levels of dye-fibre fixation (Mohan *et al.*, 2007). Textile wastewater's discharge into the environment has become a critical matter for both environmental and aesthetical reasons. It may be mutagenic, basically carcinogenic and lead to severe damages such as allergy, brain, dermatitis, skin discomfort, kidney malfunction, liver, malfunction of human's central nervous and reproductive system (Hatch, 2003). Furthermore, the coloured wastewater is extremely poisonous to the aquatic environment; they interfere in the light transmission and affect the biological metabolism activities, thereby causing ecosystem imbalances for aquatic communities (Pereira & Arruda 2003; Noorozi and Sorial, 2013).

Textile wastewater is normally trained into very close drains which later find its way to the nearby lagoons, ponds, rivers, stagnant or stream. That kind of disposal of wastewater can result in impairment to the quality of the aesthetic and biological heterogeneity of environment, aquatic eco-system, receiving water bodies. Due to these cataclysmic effects, it is very significant to ascertain distinct ways of treating this wastewater before being discharged into water bodies. In the world of today, Nigeria is one of the major consumers and producers of citrus fruits especially orange, while the orange (juices) were consumed as fantabulous means of vitamin C; its peels are disposed and send to garbage as under-utilised materials without taking care of the environment and also not considering any preventive measure to exclude the percolation of these pollutants into the underlying water channels. It is therefore very important and essential to find meaningful applications for these peels as its generation is on the increase nowadays and poses a very serious environmental concern (Akinhanmi *et al*., 2020). As a result, orange peel as agro-waste is suggested to be developed into alternative and favourable adsorbent for remediation of textile wastewater.

In the recent past, a number of treatment technologies such as coagulation/flocculation (Vandevivere *et al.*, 1998), chemical oxidation (Salem, 2001), ozonation (Baban *et al*., 2003), ion exchange process (Yu *et al*., 2001), solvent extraction (Lee *et al*., 2000), degeneration of photo catalysis (Tanaka *et al*., 2000) and adsorption process (Allen and Koumanova, 2005) have been adopted for remediation of wastewater. These treatment technologies are not affordable, inefficient and large residues are produced. Over the years, the activated carbon usage in adsorption technique has been substantiated as a very efficacious method of treating textile wastewater (Akinhanmi *et al*., 2020). The high adsorption efficiency of activated carbon, powdery or granular mode made it almost extensively utilised adsorbent for organic compounds (Alyuz and Velis, 2009). Yet, high cost and residue generation are certain challenging factors of using activated carbon adsorbents in water pollution control; hence there have been efforts in the direction of developing alternative low cost ones.

The use of agro-wastes as adsorbent presently receives more attention due to their accessibility, convenient chemical alteration, existence of good structure of porous, less disposal problem after adsorption, low cost, proficient adsorption capacity, proportionate high content of fixed carbon, and quick renewal. Agro-wastes adsorbents are economical, efficient and safe at removing various pollutants like trace metals, COD, phenol, and dyes from industrial wastewater (Salleh *et al*., 2011). Much more recently, activated carbon utilization in adsorption process has been substantiated to be a commonly employed and an effective technique for textile wastewater's treatment (Alyuz and Velis, 2009). The activated carbon from commercial source is still a costly material and for this reason, the search for economical and eco-friendly adsorbent for dye remediation in wastewater is highly essential. Locust bean pod (Bello et al., 2019) and lemon grass leaf (Ahmad et al., 2020 & 2021) among others have been studied and reported as agro-waste adsorbents used in treatment of textile wastewater. In an earlier research, the ability of orange peel to remove acid dye (Sivaraj et al., 2001), nickel (Gonen and Serin, 2012), cadmium (Akinhanmi *et al*., 2020) etc. from aqueous solutions were investigated.

Basically, Orange peel has water – soluble colloidal carbohydrates, hemi-cellulose, complex polymer fibers, green pigment with some hydrocarbons of low molecular weight (Liang *et al*., 2010). The peels are cheap, non-dangerous, non-poisonous, degradable and environmentally favourable biosorbents in wastewater treatment. This study was performed to investigate removal efficiency of colour Copper (Cu) and Zinc (Zn) from textile wastewater using carbonized orange peels (COPs). The key objectives are to determine initial absorbance and concentration, optimum values of rotating speed (in revolutions per minute, rpm), retention time, adsorbent's dosage and pH variables on percentage removal of colour, Zn and Cu from textile wastewater in a bid to assess the overall adsorbent efficiency.

Materials and Methods

Preparation of Samples

The preparation of both the orange peel adsorbent and the wastewater samples are as follows:
(i) *The raw adsorbent*: Fresh oranges were purchased from Ile-Epo market in Agbado Oke-Odo Local Government Area of Lagos State, Nigeria. Oranges were washed and peeled. The peels were washed under sterilized water to get rid of any dirt and undesirable elements. They were aseptically cut into little pieces for comfortable drying, and then dried in an oven at 100 ± 2 ^{o}C temperature for 24 hrs (Ojoawo *et al*., 2018). The dried pieces were powdered using mixer grinder and sieved using BS Sieve 10 (i.e. 2.00 mm) for uniform particle size and were stockpiled in air tight container. The prepared orange peel powder was calcined in a muffle furnace (Carbolite CWF 1200) at 300 ± 5 ^{o}C for 2 hrs at the Federal Institute for Industrial Research, Oshodi, Lagos, Nigeria following procedures of Malik (2004). The Carbonized Orange Peel (COP) powder was cooled to room temperature, washed with sterilized water till constant pH of 7 is attained and then oven dried at 105 ± 5 ^{o}C. The COP otherwise called adsorbent was sieved using BS Sieve 40 (i.e. 0.425mm) and kept in a desiccate for future use.

(ii) *Wastewater preparation*: Fresh sample of textile wastewater was collected from the Adire-Kampala market local dye industry at Itoku, Abeokuta, Ogun State of Nigeria. The samples were fetched according to the standards stipulated in Ojoawo and Udayakumar (2016) and taken directly to the laboratory for experiments. Distilled water was obtained from Food Technology Department, LAUTECH, Ogbomoso, Nigeria. Hydrochloric acid (HCl) and Sodium hydroxide (NaOH) were obtained from Labtrade Chemicals, Idi - Araba, Ogbomoso, Nigeria. The equipment used includes pH meter, UV spectrophotometer, and Atomic Absorption Spectrophotometer (AAS).

Adsorption experiment

Adsorption experiment was carried out for assessment of the efficacy of the prepared adsorbent in remediating dye wastewater. Batch adsorption experiment at room temperature was adopted to find the effects of adsorbent's dosage (0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 gram) at constant agitation rate (150 rpm), contact time (60 mins.) and pH (7.0) on the remediation of colour, Zn and Cu from textile wastewater. The pH, colour and presence of trace metals in the textile wastewater were determined before and also in the filtrate after the adsorption processes. The pH of sample was analyzed using a digital pH meter (Model KL-03l) and adjusted as required using either 0.1M of HCl or NaOH solution. The colour and the presence of Zn and Cu were established using UV spectrophotometer and AAS respectively. The Water Resources Laboratory of the Civil Engineering Department, LAUTECH, Ogbomoso, Nigeria was used for the experiments and analyses. Each of the experiments was carried out thrice and the optimum value of the adsorbent dosage determined which was then used for subsequent experiments.

(i) *Variation of Zn^{2+} and Cu^{2+} removal from textile wastewater with agitation speed, contact time, absorbent's dosage and pH*: Subsequently, solutions from the above experiments were filtered using Whatman no. 45 filter paper in preparation for determination of Zn and Cu concentrations in the filtrate. The Zn and Cu concentrations of each sample was analysed by AAS of the Central Research Laboratory, LAUTECH, Ogbomoso, Nigeria. The amount of adsorbed metals was established with Eq. (1) and the removal efficiency determined through computation of the percentage adsorption using Eq. (2) (Song *et al*., 2014; Ojoawo *et al*., 2018).

$$\text{The amount of adsorbed metal (qe)} = \frac{(\mathrm{Co} - \mathrm{Ce})\,\mathrm{V}}{\mathrm{m}} \qquad (1)$$

$$\text{Percentage removal} = \frac{(\text{Co} - \text{Ce})\ 100}{\text{Co}} \qquad (2)$$

Where qe is the adsorption capacity at equilibrium (mg of ions/g of orange peels), V is the volume of the aqueous solution (mL), Co is the concentration before adsorption (mg/L), Ce is the equilibrium concentration after adsorption (mg/L) and m is the mass in gram of the adsorbent.

(ii) *Variation of colour removal from textile wastewater with adsorbent's dosage, optimum agitation speed and time*: 100 ml of textile wastewater was maintained at pH of 7.0 in a reagent bottles (250 ml) and variants dosage of 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 gram of adsorbent was added to it. The solutions were then kept in rotary machine at the optimum agitation speed for the optimum time to enhance effectual mixing. Then the reaction mixtures in the reagent bottles were maintained undisturbed for 1 hr. in other to allow settlement of the precipitation formed. This precipitate was segregated from the mix by filtration through 0.45 µm Whatman filter paper. Initial sample without adsorbent was used as control. The filtrate was studied for percentage colour removal and the optimum dosage for colour removal was determined.

(iii) *Variation of colour removal from textile wastewater with pH, optimum agitation, time and adsorbent's dosage*: The textile wastewater was examined at different pH of 2.0, 4.0, 6.0, 8.0, and 10.0. The optimum dosage of adsorbent was added to 100 ml of the textile wastewater in the 250 ml reagent bottles. The solutions were kept in rotary machine at the optimum RPM for the optimum time to enhance effectual mixing. The bottles having retorted mixed substance was left untroubled for 1 hr. to enable settlement of precipitation formed. The formed precipitate was segregated from the mix using 0.45 µm Whatman filter paper (i.e. filtration). Initial sample without adsorbent was used as control. The filtrate was examined for percentage colour removal. % colour removal was determined using the initial and final absorbance values (i.e. before and after treatment values) for the textile wastewater samples and thus, Standard calibration curve was prepared. The % colour removal was established by the formula in Eq. (3) (Javaid, 2013).

$$\%\ \text{Colour removal} = \frac{(\text{Co} - \text{Ce})\ \text{x}\ 100}{(\text{Co})} \qquad (3)$$

(iv) *Variation of colour removal from textile wastewater with agitation*: 100 ml of the textile wastewater was maintained at pH 7.0 inside 250 ml reagent bottles and 1 gram of adsorbent was added to it. The solution was then kept in rotary machine at variant speeds of 50, 100, 150, 200 and 250 rpm for 60 min in each case to enhance effectual mixing and causes formation. The reagent bottles housing retort mixture were being put in uninterrupted condition for 1 hour to allow the settlement of the formed precipitation. The settled precipitate was separated through its filtration through 0.45 µm Whatman filter paper. Initial sample without adsorbent served as control. Filtrates were analysed for the maximum concentration of dye absorbed and percentage colour removal, while the optimum agitation speed in rpm was also determined.

(v) *Variation of colour removal from textile wastewater with contact time*: The solutions were prepared as in (iv) then kept in a rotary machine at the optimum agitation for a variant time of 20, 40, 60, 80 and 100 minutes to enhance effectual mixing and causes formation. Standard adsorption procedure was followed and the settled precipitate segregated from the mix by filtration. All the samples at the varying contact time were analyzed and compared with the initial sample to determine the % removal of dye and the effects of contact time. The optimum time for the colour removal percentage was determined.

Tests

(i) *Fourier Transform Infrared (FTIR) characterization of the adsorbent*: The functional groups of the Orange peel biosorbent and adsorbent were determined by FTIR using Infrared Spectrophotometer (BUCK M530 model series) at the Central Research Laboratory of LAUTECH, Ogbomoso, Nigeria. Infrared Spectrophotometer is an exceptionally mighty instrument for distinguishing the functionalities' presence e.g. alkane, aromatic compounds, amino compounds, Carbonyl, Hydroxyl etc. The molecule's vibration spectra are observed to be a distinctive physical property. The most useful region of the infrared radiation extends from above 2.5 to 16 microns (1 micron = 1 micrometer = 10-6 meter). The wave number of a particular radiation is the number of waves per centimeter, which is simply one divided by the wavelength (λ) in centimeter (Hassan and Abiola, 2018).

(ii) *UV Spectrophotometer*: Generally, the dye wastewater's concentration was established spectrophotometrically at maximum wavelength of 580 with UV-vis spectrophotometer with the initial absorbance of 0.320 Abs.

(iii) *Atomic Absorption Spectrophotometer (AAS)*: The wastewater (10ml) and nitric acid (10 ml, acting as a catalyst) was carefully mixed in a 50ml beaker and heated for 30 minutes at 100˚C inside fume cupboard. Sterilized water added to the cooled mixture after being removed from the fume cupboard in other to make it up to 100ml, filtered and the filtrate was analysed using AAS. The filtrate samples from the batch adsorption experiments were initially digested in other to breakdown their elements' complexities. The AAS with model number PG-990 of the College of Agriculture, University of Osun, Ejigbo Campus, Osun State, Nigeria was used (Ojoawo and Udayakumar, 2016).

Adsorption Isotherm

Adsorption isotherm is the relationship established by determining the quantity of material adsorbed as concentration of adsorbent basis at steady temperature. Quantity of adsorbed adsorbate is nearly continuously normalized by the adsorbent's mass for various layers' comparison.

(i) *Langmuir Isotherm*: It based on the occurrence of adsorption at particular homogeneous sites of the adsorbent. Adsorption's monolayer is adopted on the surface of the concerned adsorbent. It is as presented in Eq. (4) (Langmuir, 1918).

$$\frac{C_e}{q_e} = \frac{1}{q_m}.\frac{1}{K_L} + \frac{C_e}{q_m} \qquad (4)$$

Where qe is adsorbed concentration at equilibrium (mg/g), qm is maximum capacity of adsorbent for adsorbate corresponding to the complete monolayer coverage (mg/g), Ce is concentration at equilibrium (mg/L) and KL is Langmuir isotherm constant associated with energy of adsorption.
The Langmuir constants qm and KL are calculated from the slope and intercept of plot between 1/qe versus 1/Ce. Separation factor (R_L), which shows the adsorption efficiency was calculated using Eq. (5).

$$R_L = \frac{1}{1 + K_L Co} \qquad (5)$$

The value of R_L equals > 1, 1, $0 < R_L < 1$ and 0 means the adsorption is linear, unfavourable and favourable and irreversible respectively (Chen and Zhao, 2009; Farooq *et al*., 2010).

(ii) *Freundlich Isotherm*: It expatiates on the correlation between perfect and non-perfect adsorption with its application to heterogeneous surface while there is an interaction among the molecules adsorbed. Its empirical formula is presented in Eq. (6) (Freundlich and Heller, 1939).

$$\text{Log } q_e = \text{ Log } K_f + \frac{1}{nf} \text{ Log } C_e \tag{6}$$

The plot of Log qe versus Log Ce will give the slope 1/n and intercept Kf {(mg/g) / (L/g) n}. Kf is the Freundlich constant related to adsorption intensity of adsorbents (mg/g) and n is the Freundlich exponent. Here, Kf and n are defined as the constants for the adsorption capacity and intensity of adsorption respectively. The slope (value of 1/n), which always lie between 0 and 1 is a measure of adsorption intensity. If 1/n = 1 then this shows that the existing partition between the two phases are independent of the concentration. If value of 1/n is less than one, it depicts a normal adsorption, i.e an adsorption through chemical process). On the other hand, the value of 1/n being greater than one denotes cooperative adsorption, passing through a physical process (Matouq *et al.,* 2015). Meanwhile if n however lie between one and ten it is an indication of a favourable adsorption process.

Adsorption kinetics

There is need for kinetic to facilitate adsorption systems' design and rate of reaction's control. The orange peel adsorption data can be analysed by kinetic studies that will result in determination of the capable adsorption mechanisms. Pseudo-first and pseudo-second order kinetic models were used to explain the adsorption processes in this study, which hinges on the physicochemical attributes of the adsorbent.

(i) *Pseudo-first order kinetic model*: It is broadly expressed in linear form according to Lagergren as presented in Eq. (7) (Markandeya *et al*., 2015, Farhan *et al*., 2012).

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

The K_1 and qe were evaluated from slope and intercept of straight line of plot Log (qe - qt) and t.
(ii) *Pseudo-second order kinetic model*: It is premised on adsorption capacity of adsorbate layers employed in analysing chemisorption's kinetics rate. It is utilised in a linear form of Eq. (8).

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

The K_2 and qe were evaluated from slope and intercept of straight line of plot t/qt and t. The fixed rate of adsorption of pseudo-first and second order kinetic models are K_1 and K_2, respectively, qt is the quantity of colour or metal adsorbed at particular time t (minute), qe is the quantity of colour or metal adsorbed at equilibrium.

Results and Discussion

FTIR characterization results of the adsorbent: Figure 1 portrays the functional groups of the orange peel sample using FTIR. Transmittance peaks at 3355 and 3239 1/cm shows the intra-molecular O-H bonds while the bands at 2832, 2801, 2707 1/cm shows the asymmetric and symmetric C-H respectively. The free carbonyl group (C=O) was seen at 1781 1/cm while the C=C aromatic of the orange peel sample was seen at 1558.1. The C-H bend vibrations were shown at 1407, 1268 and 1210 1/cm respectively. The increased boiling points in comparison to their parent alkanes was due to the presence of an –OH group alcohol. The covalent bond of C-H bond portrays sharing of carbon in its outer valence electrons with hydrogens. The polarity of carbonyl group, C=O bonded compounds increase both the melting and boiling points (Hassan and Abiola, 2018). All of these results are pointing to strong bonding characteristics of the orange peel adsorbent.

The initial absorbance and concentration of colour and metals in the textile wastewater sample: The initial pH of the textile wastewater is 10.0 at maximum wavelength of 580 with UV spectrophotometer and absorbance of 0.320 Abs. The selected trace metal (Zinc - Zn^{2+} and Copper - Cu^{2+}) analysis as carried out on the dye sample detected an appreciable concentration of Zn^{2+} (0.2456 mg/L) and Cu^{2+} (0.2392 mg/L).

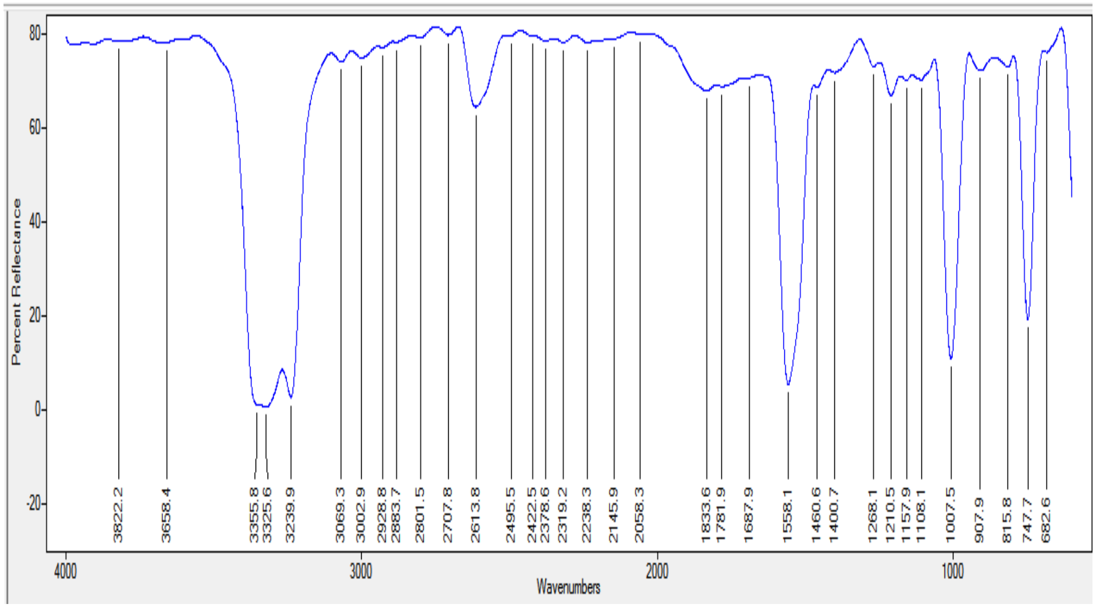

Figure 1. FTIR analysis Results on the Orange peel adsorbent

Effect of rotating speed on percentage removal of Colour, Zinc and Copper: The variation of colour, Zinc (Zn^{2+}) and Copper (Cu^{2+}) removed from textile wastewater with reference to rotating speed (in rpm) are represented in Figure 2. Maximum removal of colour, Zn^{2+} and Cu^{2+} values were 41.56, 90.47 and 78.97 % respectively, which occured at optimum values of 100 rpm for colour and 250 rpm for both Zn^{2+} and Cu^{2+} as indicated by the circle on each of the graphs. From the obtained results, it could be seen that the percentage of colour removed increases sharply as the rotating speed increased in the first 100 rpm perhaps as a result of enormous number of sites initially vacated. The removal efficiency later decreased with the increasing rotating speed, which indicated that there was no increase in colour removed with additional increase in the rotating speed. Initially, there was rapid removal percentages of Zn^{2+} and Cu^{2+} and also increased with contact time. This could be due to amount of active porous site available and the maximum concentration of Zn^{2+} and Cu^{2+} in the solution, thus enhances the maximization of Zn^{2+} and Cu^{2+} adsorption on adsorbent surface. Additional rotation makes available the vigour required to transport the Zn^{2+} and Cu^{2+} from the whole of the solution to the adsorbent's active sites through reduction of the resistance to mass transfer between adsorbent and whole phase as expressed by Salem (2001) and Malik (2004).

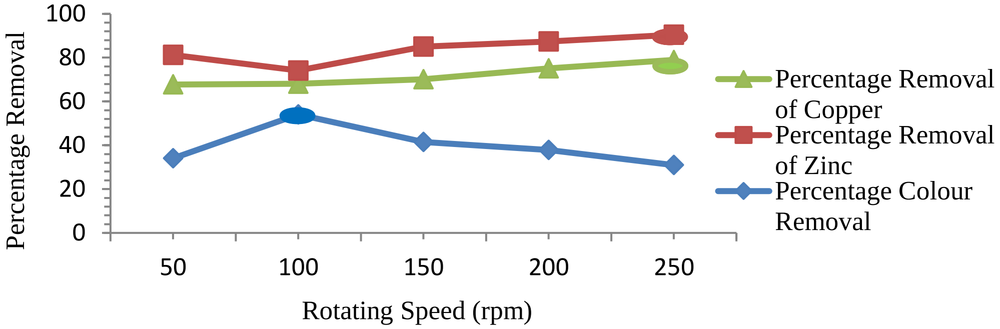

Figure 2. Effect of rotating speed on percentage removal of Colour, Zn and Cu

Effect of contact time on percentage removal of Colour, Zinc and Copper: Variations of colour, Zinc (Zn^{2+}) and Copper (Cu^{2+}) removal from dye wastewater with time at optimum agitation speed of 100 rpm for colour and 250 rpm for Zn^{2+} and Cu^{2+} respectively are shown Figure 3. The maximum colour, Zn^{2+} and Cu^{2+} removal of 50.31, 93.85 and 72.82% occurs at optimum time of 40, 60 and 40 minutes respectively. The percentage of colour removal as a function of time indicated that, the percentage removal increased swiftly from the contact time of 20 - 40 minutes and decreased promptly as the contact time increased. This can be explained by the fact that initially, the quantity of sites on the surface is very large which allows adsorption to take place very easily. But with the passage of time, the active sites get saturated thereby reducing the rate at which adsorption occurs. It was noted that the optimum contact time of 40 minutes corresponds to the optimum contact time of Copper. Nonetheless, variation was observed among the percentage removal of Zn^{2+} and Cu^{2+}.

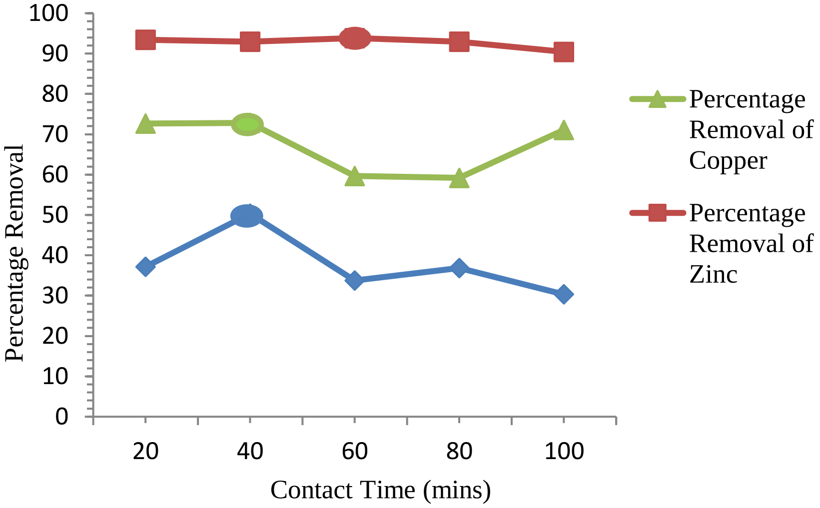

Figure 3. Effect of contact time on percentage removal of Colour, Zinc and Copper

Though, beyond the optimum contact time of the metals, further increase in contact time has no significant effect on the metal removal. This could be attributed to the accumulation of metal ions on the vacant sites or the solution itself is saturated, so increase in the rate of adsorption ceases (AsmaHanif *et al.*, 2009). Therefore, further increase in contact time did not enhance the metal removal and thus, the optimum retention time is selected as reported by Salem (2001), Akinhanmi *et al*. (2020). The findings are also corroborated by Ojoawo and Udayakumar (2016).

Effect of adsorbent's dosage on percentage removal of Colour, Zinc and Copper: Variations of colour, Zinc and Copper (Zn^{2+} and Cu^{2+}) removal from dye wastewater with adsorbent dosage (carbonized orange peel) at optimum agitation of 100 rpm for colour and 250 rpm for Zn^{2+} and Cu^{2+} and optimum contact time of 40, 60 and 40 mins respectively are shown in Figure 4. The maximum efficiencies of the adsorbent for colour, Zn2+ and Cu2+ removal of 70.93, 99.84 and 75.75% occurs at optimum dosage of 2.5, 0.5 and 3.0 g respectively. Adsorbent's dosage plays a fundamental role in adsorption process (Salleh *et al*., 2011). The percentage removal of colour was found to increase as the adsorbent's dosage increases. This could be attributed to the increase in surface area and amount of active sites in the adsorbent. Moreover, with further increase, there was an observed decrease in the percentage removal of colour due to an increase in adsorbent dosage beyond maximum adsorption capacity which might be due to the congestion of adsorbent particles beyond the optimum dose (Garg *et al*., 2004). In relation to metals, it was observed that Zn^{2+} has virtually equal percentage removal values with increasing adsorbent's dosage from 0.5 to 3.0 g while Cu^{2+} metals displayed varying removal efficiencies with dosage. This observation is in relation to Ojoawo and Udayakumar (2016) findings on remediation and adsorption studies of lead and copper in fresh foundry wastewater using AC-250.

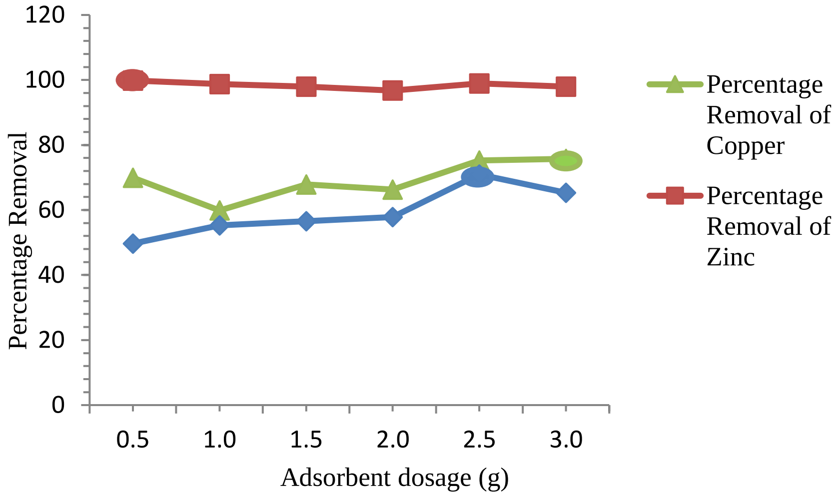

Figure 4. Effect of adsorbent dosage on percentage removal of Colour, Zinc and Copper

Effect of pH on percentage removal of Colour, Zinc and Copper: Variations of colour, Zinc (Zn^{2+}) and Copper (Cu^{2+}) removal from dye wastewater with pH at optimum agitation of 100 rpm for colour and 250 for Zn^{2+} and Cu^{2+}, optimum time of 40, 60 and 40 mins. respectively and at optimum dosage of 2.5, 0.5 and 3.0 g respectively are shown in Figure 5. The original pH of the dye wastewater has a very noteworthy effect on the adsorbent surface characteristics as well as the degree at which the dye molecules ionize and thus, it becomes utmost to examine the influence that pH has on the adsorption process (Salleh *et al*., 2011). The maximum colour, Zn^{2+} and Cu^{2+} removal of 87.18, 99.76 and 93.81% occurs at optimum dye sample pH of 10, 4 and 2 respectively. In the trials, as the pH of the solution increase the removal efficiency of the colour also increases. The higher adsorption at pH 10 could be due to interaction between the positively charged dyes cations and the bio-active ingredients that may be present in the adsorbent.

Moreover, the pH is one of the main variable parameters in adsorption process which affects the removal efficiency of Zn^{2+} and Cu^{2+}. It was observed that Zn^{2+} has virtually equal percentage removal values with increasing pH from 2 to 10 while Cu^{2+} metals displayed varying removal efficiencies with pH. The noted percentage removal of metal ions may be attributed to the fact that the adsorbent surface is already de-protonated and is negatively charged, hence attraction between the positively metal cations occurred which increases the availability of Zn^{2+} and Cu^{2+} for adsorption as corroborated by Lohani *et al.*, (2008); Adetoro and Ojoawo (2020).

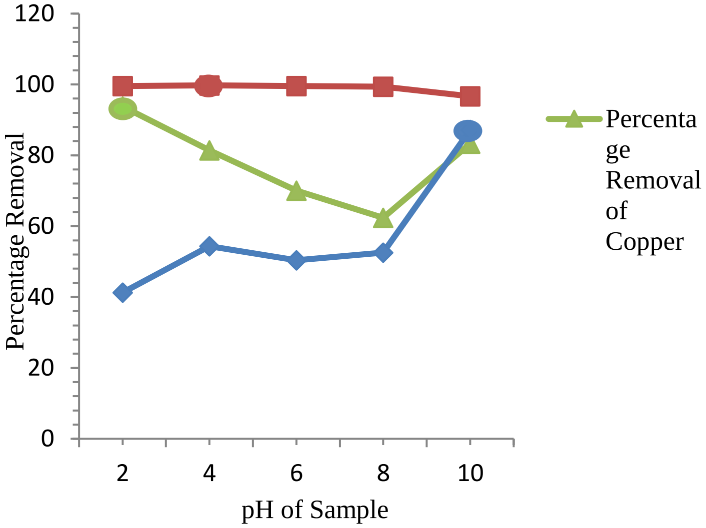

Figure 5. Effect of pH on percentage removal of Colour, Zinc and Copper

Adsorption Isotherms

The values of the constants of the two isotherms, namely Langmuir and Freundlich were given in Table 1.

Table 1. The Values of Constants for the Two Adsorption Isotherms

Constants	Colour		Zinc		Copper	
	Langmuir	Freundlich	Langmuir	Freundlich	Langmuir	Freundlich
qm/(1/n)	-19.84	2.1263	1.1121	-0.5089	-17.57	1.3473
K_L/ K_f	-2.864	991.06	-2997.3	0.8362	-4.948	377.22
R^2	0.5193	0.5827	0.4418	0.6464	0.3804	0.1721

Langmuir Isotherm model: The results obtained from Langmuir isotherm model for colour, zinc and copper with the plot of 1/qe against 1/Ce are summarized in Figure 6. Equations of straight lines were obtained. Constants q_m and K_L were calculated by using equation 3 and results have been tabulated in Table 1. In order to find efficiency of adsorption process, separation factor (R_L) was calculated using equation 4. The R_L values for colour, zinc and copper were 11.973, 0.0 and 0.0, respectively. The value of R_L for colour confirms that the adsorption is unfavourable since it is greater 1. Meanwhile, the value of R_L for the zinc and copper confirms that the adsorption is irreversible (Chen and Zhao 2009; Farooq *et al*., 2010).

Freundlich Isotherm model: For Freundlich isotherm, the equilibrium data obtained was plotted between log qe versus Log Ce. The plot of Log qe versus Log Ce gives straight line graphs with correlation coefficients (Figure 7). Constants K_f and 1/n were calculated by using equation 5. The values of 1/n for colour, zinc and copper were 2.1263, -0.5089 and 1.3473, respectively. The value of 1/n for colour and copper being above one indicates a cooperative adsorption through physical process) (Matouq *et al*., 2015). On the other hand, the value of 1/n for zinc tends toward zero; hence, it depicts an irreversible adsorption (Ghasemi and Gholami, 2014).

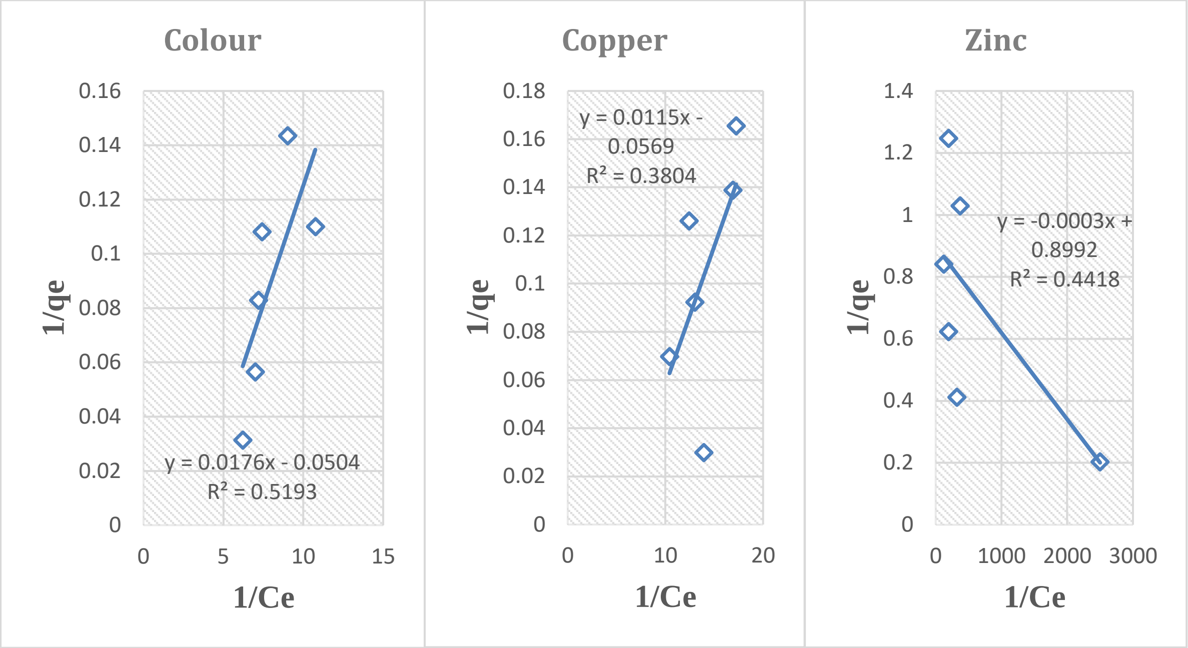

Figure 6. Langmuir isotherm model for Colour, Zinc and Copper adsorption

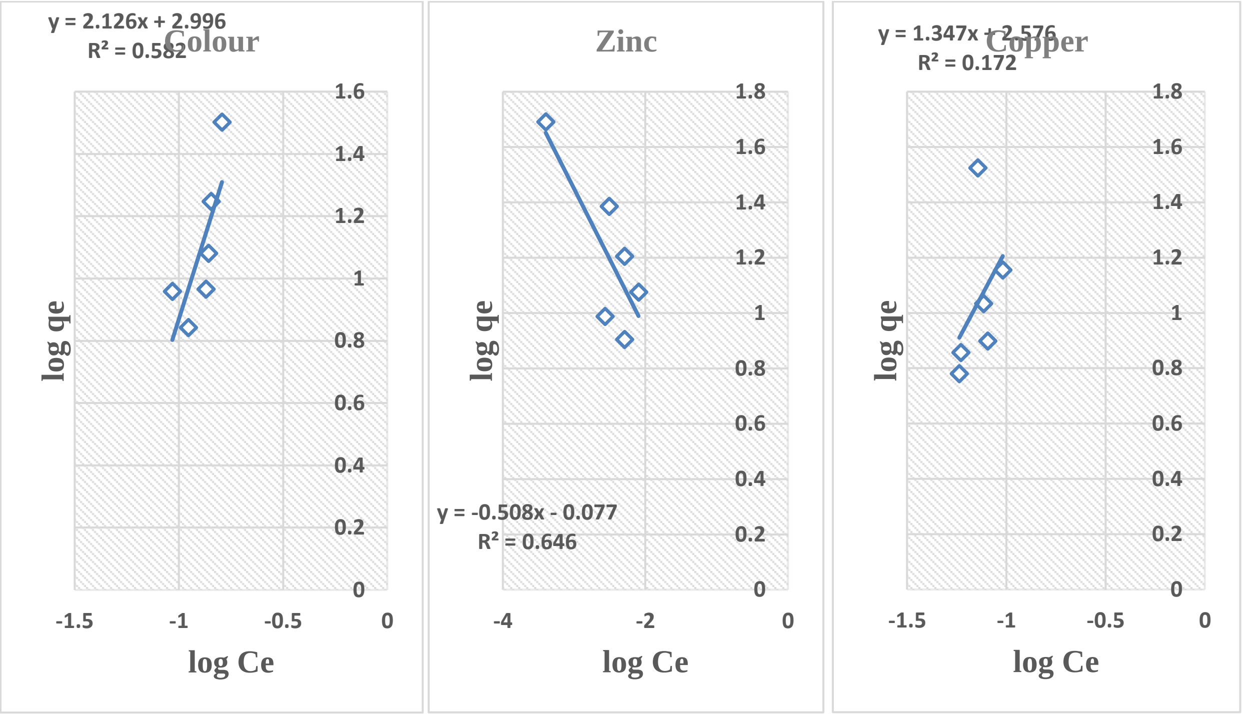

Figure 7. Freundlich isotherm model for Colour, Zinc and Copper adsorption

Generally, the results of colour and zinc removal showed higher correlation coefficient (R^2) values for the Freundlich model, which confirmed better fitting of this model to the experimental data. Meanwhile, the results of copper removal showed the higher correlation coefficient (R^2) values for the Langmuir isotherm model, which confirmed better fitting of this model to the experimental data. The lower value of correlation coefficient in either case could be suggested that either of these models did not accurately describe the correlation between the amounts of adsorbed colour or metal ions and their equilibrium concentrations in the solutions (Pandey *et al*., 2017). Roshan (2015) has also investigated removal of Congo red dye from water using orange peel as an adsorbent and found Freundlich isotherm model a better fit in the adsorption isotherm model. Fitting of data to Freundlich model shows that adsorption of the dye follows heterogeneous polylayer coverage of the adsorbate on the adsorbent surface (Freundlich and Heller, 1939) and to Langmuir isotherm model indicates that the adsorbent surface is uniform and homogeneous and that the adsorption reaction results in the formation of a monolayer of adsorbed molecules (Langmuir, 1918).

Adsorption kinetics

This reflects the relationship between rate of sorption and contact time. The values of K_1 and K_2 as subjected to the pseudo first and second order kinetic model were obtained from the slopes of the plot of Log (qe − qt) versus 't' (Figure 8) and't/qt' versus 't' (Figure 9) respectively. Equations of straight lines were obtained and the constants (K_1, K_2 and q_e) were calculated using equation 7 and 8 respectively. The results show that the values of correlation coefficients (R^2) from the pseudo-first order kinetic model were low compared to the pseudo-second order kinetic model, which suggested that the adsorption of both colour and metal ions departed significantly from the pseudo-first order kinetic model and could not explain the adsorption mechanism of colour, zinc and copper onto the carbonised orange peels. These results indicated that the adsorption system studied followed the pseudo-second order kinetic model for both colour and metals, with correlation coefficient in both cases being close to one. The pseudo-second order kinetic mode was based on the fact that chemical sorption controls the sorption rate (Ding *et al*., 2011). If kinetic model fits well to pseudo-second order reaction plot by giving R^2 value close to one, it indicates an inclination towards chemisorption.

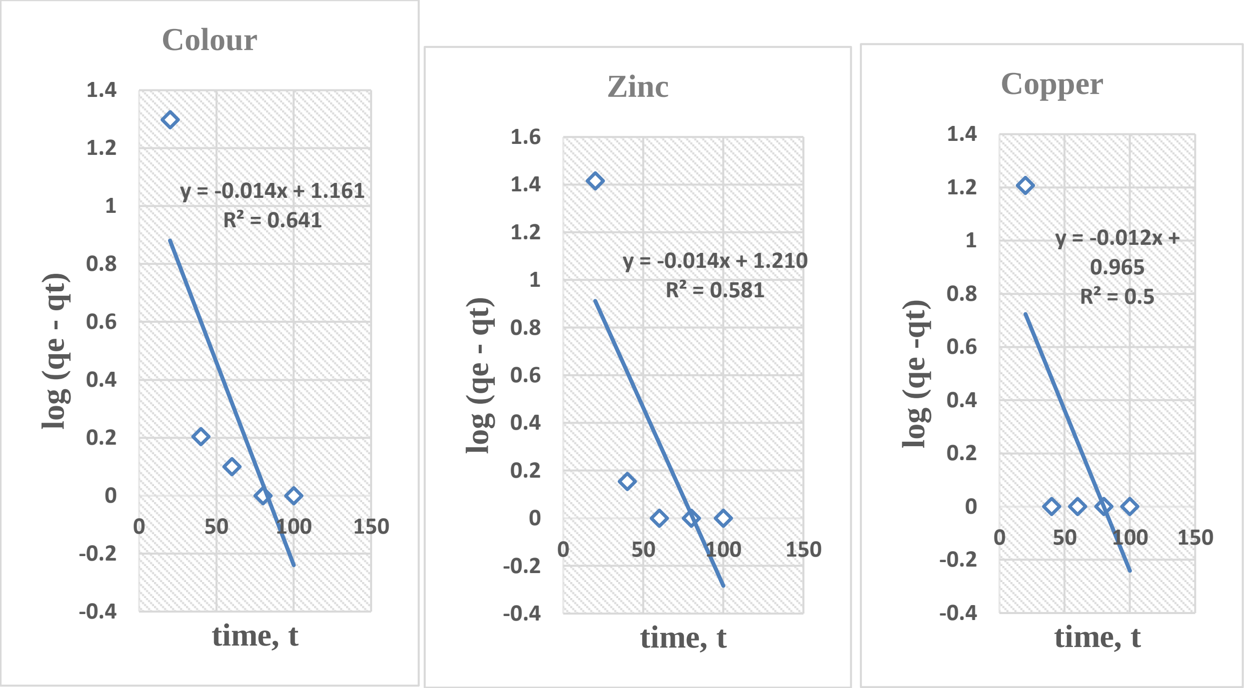

Figure 8. Pseudo-first order model simulation of colour, zinc and copper by the carbonized orange peel

However, if pseudo-first order reaction plots by giving R^2 value close to unity, it indicates that the reaction is more inclined towards physisorption. Meanwhile Ojoawo and Udayakumar (2016) found pseudo-second order fit for the remediation and adsorption studies of Pb^{2+} and Cu^{2+} in fresh foundry wastewater using AC-250 on the basis of higher R^2. Again, Matouq *et al.,* (2015) investigated adsorption kinetics and modelling for heavy metal removals and found pseudo-second order fit for it on basis of higher R^2.

Table 2 summarizes the general findings from this adsorption study of Orange Peel on textile dye wastewater.

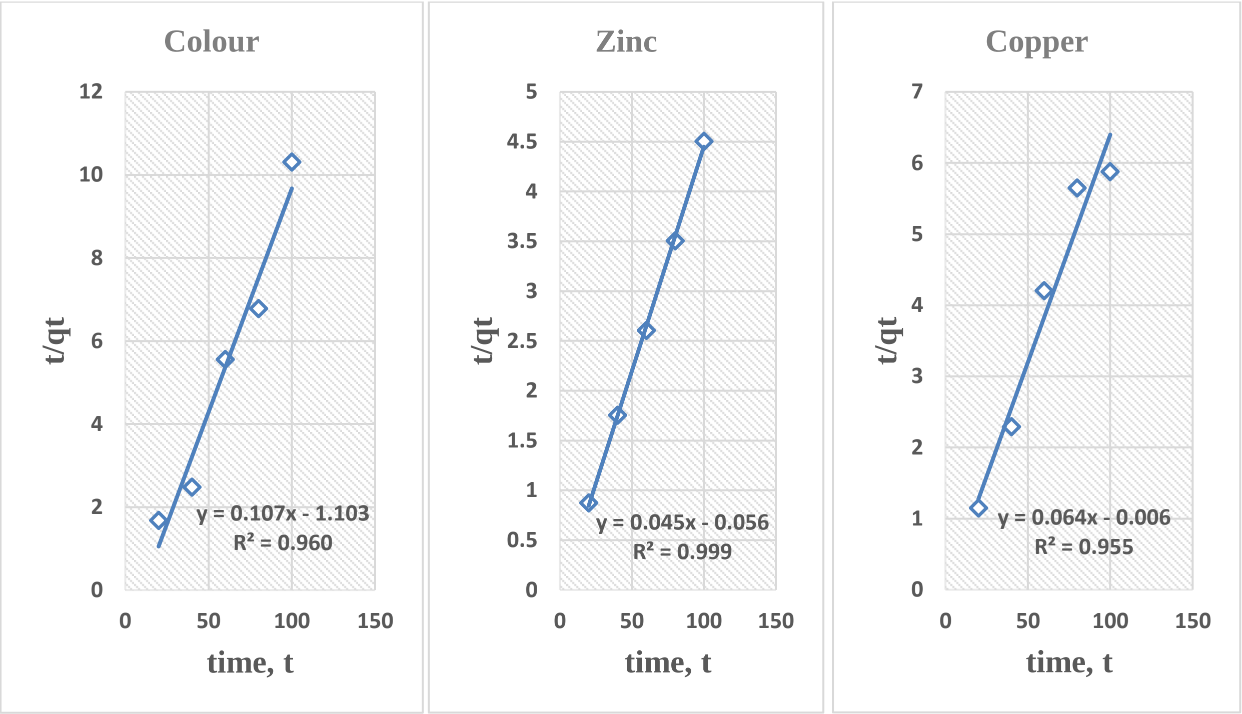

Figure 9. Pseudo-second order model simulation of colour, zinc and copper by the carbonized orange peel

Table 2. Summary of the findings from the adsorption study

Variable	Optimum Value			Maximum % Removal		
	Colour	Zn2+	Cu2+	Colour	Zn2+	Cu2+
Rotating speed	100rpm	250rpm	250rpm	54.06rpm	90.47rpm	78.97rpm
Contact time	40mins	60mins	40mins	50.31	93.85	72.82
Adsorbent dosage	2.5g	0.5g	3.0g	70.93	99.84	75.75
pH	10	4	2	87.18	99.76	93.81

Conclusion

Carbonized orange peel (COP), an agro waste shows significant adsorption capacity for the remediation of colour from textile wastewater. Moreover, the carbonized orange peel was also most efficient in the removal of Zn^{2+} and Cu^{2+} under standard parameters and suitable experimental conditions. The study concludes as follows:

i. Carbonized orange peel is highly effective in the remediation of colour, Zn^{2+} and Cu^{2+} from textile wastewater. Orange peels being readily available at no or low cost can be carbonized and serve as a suitable cheap and environmentally friendly adsorbent in colour and metal ions' removal from textile wastewater

ii. Adsorption isotherms suggest that only the copper adsorption is optimum and fits well with Langmuir isotherm

iii. The adsorption behaviour of both the colour and the metal ions was best demonstrated by kinetic model of pseudo-second order with high correlation coefficient

iv. Moreover, the study outcome can also be valuable for designing and devising a frugally low-cost treatment process plant for the remediation of dyes and trace metals of wastes from industries.

Carbonized orange peel (COP) is therefore recommended as an adsorbent for textile wastewater's treatment before discharging into the environment. It could be employed as a substitute to the costly commercial adsorbents for the colour and trace metals' removal.

Nomenclatures

C_e	equilibrium concentration after adsorption, mg/L
C_o	concentration before adsorption, mg/L
K_1 and K_2	the adsorption rate constants of pseudo-first-order and pseudo-second-order kinetic models
K_f	Freundlich constant related to adsorption intensity of Adsorbents, mg/g
K_L	Langmuir isotherm constant associated with energy of Adsorption
n_f	Freundlich exponent
q_e	adsorbed concentration at equilibrium, mg/g
q_m	maximum capacity of adsorbent for adsorbate corresponding the complete monolayer coverage, mg/g
R^2	correlation coefficient
$1/n$	a measure of adsorption intensity (ranges between 0 and 1)

Abbreviations

AC-250	Activated Carbon grade 250
AAS	Atomic Absorption Spectrophotometer
BOD	Biochemical Oxygen Demand, mg/l
COD	Chemical Oxygen Demand, mg/l
FTIR	Fourier Transform Infrared Spectroscopy
pH	degree of alkalinity or acidity
RPM	Revolutions Per Minute

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