Scientific African 3 (2019) e00078

Contents lists available at ScienceDirect

Scientific African

journal homepage: www.elsevier.com/locate/sciaf

# Discoloration of methylene blue and slaughter house wastewater using maize cob biochar produced using a constructed burning chamber: A comparative study

C. Tsamo[a,b,*], M. Assabe[a], J. Argue[a], S.O. Ihimbru[b]

[a] Department of Chemistry, Higher Teachers' Training College Maroua, P.O. Box 55 Maroua, Cameroon
[b] Department of Agricultural and Environmental Engineering, College of Technology, University of Bamenda, P.O. BOX 39 Bambili, Cameroon

ARTICLE INFO

*Article history:*
Received 12 February 2019
Revised 29 March 2019
Accepted 8 May 2019

*Keywords:*
Batch process
Biochar
Maize cob
Methylene blue
Slaughter house waste water
Filtration

ABSTRACT

A comparative study on the discoloration of methylene blue (MB) and slaughter house waste water (SHW) using maize cob biochar produced by a laboratory constructed burning chamber was undertaken in this study. Contact time, pH, initial MB and SHW concentrations, mass of biochar and temperature were used to evaluate the efficiency of the biochar in discoloring MB and SHW in batch process. A biochar/sand filtration system was also used to study the discoloration of MB and SHW in continuous filtration. Equilibrium was attained in 15 min with 100% discoloration for SHW and 64% for MB. Maximum discoloration occurred at pH 4 and 0.05 g biochar for SHW and at pH 8 and 0.15 g biochar for MB. MB discoloration decreases with increase initial concentration while SHW discoloration increases with increase initial concentration. Both SHW and MB discoloration decreases with increase in temperature attaining 0% for SHW at 60 °C. Pseudo-second order kinetic model best describe the discoloration of MB and SHW. Langmuir, Freundlich Dubinin-Radushkevich and Temkin isotherm models describe the discoloration of MB but only Langmuir and Temkin isotherm models describe the discoloration of SHW. Slaughter house waste water is easily discolored than methylene blue in batch process as evident from calculated Langmuir equilibrium constant b (1916.71 L/mg for SHW and 0.69 L/mg for MB), Temkin equilibrium constant $A_T$ (0.98 L/mg for SHW and $4.1 \times 10^{-9}$ L/mg for MB) and Langmuir separation factor ($R_{L;}$ $5.2 \times 10^{-5}$ for SHW against 0.13 for MB). The discoloration process is physical, exothermic and less spontaneous with increasing temperature. A biochar/sand mixture filtration is more efficient in discoloring MB than SHW. Maize cob biochar can effectively be used to remove colour from methylene blue containing waste water and slaughter house waste water using low-cost materials in batch and column processes.

© 2019 The Authors. Published by Elsevier B.V. on behalf of African Institute of Mathematical Sciences / Next Einstein Initiative.
This is an open access article under the CC BY license.
(http://creativecommons.org/licenses/by/4.0/)

* Corresponding author at: Department of Chemistry, Higher Teachers' Training College Maroua, P.O. Box 55 Maroua, Cameroon
*E-mail address:* tcornelius73@yahoo.com (C. Tsamo).

https://doi.org/10.1016/j.sciaf.2019.e00078
2468-2276/© 2019 The Authors. Published by Elsevier B.V. on behalf of African Institute of Mathematical Sciences / Next Einstein Initiative. This is an open access article under the CC BY license. (http://creativecommons.org/licenses/by/4.0/)

## Introduction

Colour is one of the indicators of water pollution. The presence of colour in water sources may originate from the use of dyes in the textile, electroplating, paper, food, plastic and tanneries industries and organic matter from slaughter house waste water all of which consume much water for their different operations [1–3]. 29% of the total freshwater used in the agricultural sector worldwide is consumed by the meat processing industry alone [3]. The presence of dyes in water bodies is becoming a serious environmental problem because most dyes are toxic in nature and further undergo anaerobic degradation to form carcinogens and other toxins [4]. Equally, highly coloured wastewater has a negative impact on the photosynthesis of plants affecting their growth and the entire aquatic life because it blocks the penetration of sunlight and oxygen in to the interior of the water body [4,5]. Particularly, water pollution from slaughterhouses is becoming a serious problem in developing countries like Cameroon because the majority of existing slaughter houses are actually slaughter slabs (traditional slaughterhouses) where there is total lack of any hygienic measures or management of generated waste water [6]. After slaughtering, nearby rivers are often contaminated with blood, horns, hair, hooves and large amounts of solid waste from the paunch and intestines resulting in high coloration of the receiving water bodies [7]. An Average of 213 cows are slaughtered in fifteen traditional slaughterhouses of fifteen local council areas of the three Northern regions of Cameroon per day [6] sending all their wastes to scarce surrounding water bodies. Outbreaks of epidemics linked to water quality have been very common in these regions which have a sahelian climate with scarce water sources [8]. The need to eliminate colour from water sources is therefore imperative. Due to the fact that dyes are optically and thermally stable resulting from their complex aromatic structure, treatment of wastewater containing dyes is very difficult [9]. Moreover, dyes are very resistant to chemical, biochemical and photochemical degradation [10]. There is therefore need to improve these treatment processes using easily available technology and materials.

The method of physical separation by adsorption is currently widely used to remove pollutants from wastewater. The efficiency of the removal by this process is highly dependent on the properties of the solid adsorbent used. Some of these properties include reactivity, pollutant selectivity, easy availability and low cost, ability not to generate secondary toxic sludge and ability to remove different types of pollutants at low and high levels. There is a continuous search for locally available and low cost materials that can help provide safe drinking water to local communities particularly that lack access to electricity for modern treatment technologies.

Research on the use of agricultural waste materials such hazelnut shell, saw dust, sunflower stalk, sunflower seed shells, mandarin peelings, orange peel, maize cob, soy meal hull, bagasse pith, sugarcane dust etc. as adsorbent for dyes removal from wastewater is on the rise worldwide [11]. However, the adsorbent properties of these biowaste materials such as porosity, specific surface area, cation exchange capacity, and surface functional groups can be improved by converting them to other materials such as biochar (obtained in a low-cost preparation process compared to that of activated carbon) [12,13]. It is a carbon rich form of charcoal produced by pyrolysis under limited oxygen conditions from waste biomass at temperatures between 350 and 800 °C [12,14]. Biochar has been demonstrated as a very efficient adsorbent for the removal of organic pollutants from aqueous solutions [12,15]. The waste biomass is very abundant especially in developing countries where the principal activity is agriculture. In Cameroon, 141 066.44 tons of dry maize cobs are produced annually in the three Northern Regions of Cameroon against 362,508.74 tons at national level [16]. In this study a comparative study was carried out to investigate the effectiveness of discoloration of methylene blue (MB) and slaughter house waste water (SHW) using biochar obtained from maize cobs in batch and continuous filtration systems. A system was designed in the laboratory to prepare the biochar. The batch experimental data was used to establish different isotherms and kinetic models while breakthrough curves were used to described column adsorption. MB was used because it has been widely used as model contaminant to characterize the suitability of various solids for water treatment [17].

## Material and methods

### *Construction of biochar burning chamber*

An inner chamber with a height of 31 cm and circumference of 118 cm was formed by bending a metal sheet cut in dimensions of 120 cm by 25 cm. An outer chamber formed with metal sheet of dimension of 155 cm by 31 cm was used to surround the inner chamber to limit air flow in to the inner or burning chamber (Fig. 1a). Iron rods cut into lengths of 37 cm were attached 5 cm from the bottom of the inner chamber by welding to hold the biomass and the bottom sealed with a spherical metal sheet (Fig. 1b). A metal sheet shaped spherical serving as lid cover was welded on top of the chamber and perforated to provide space for attachments of the chimney. The chimney was also attached to the lid of the chamber by welding. The chimney is to provide outlet for smoke. The entire design was then painted with grey paint (Fig. 1c) which provides a neutral, disappearing background.

### *Production of biochar*

Burning of the maize cobs was carried out using the constructed biochar burning chamber (Fig. 1c). 3 kg of dried maize cobs collected from the warehouse of the Cameroon institute of Agricultural Research and Development (IRAD) Bambui were placed in the burning chamber, ignited from the top (Fig. 2) and closed with the lid and allowed for pyrolysis to

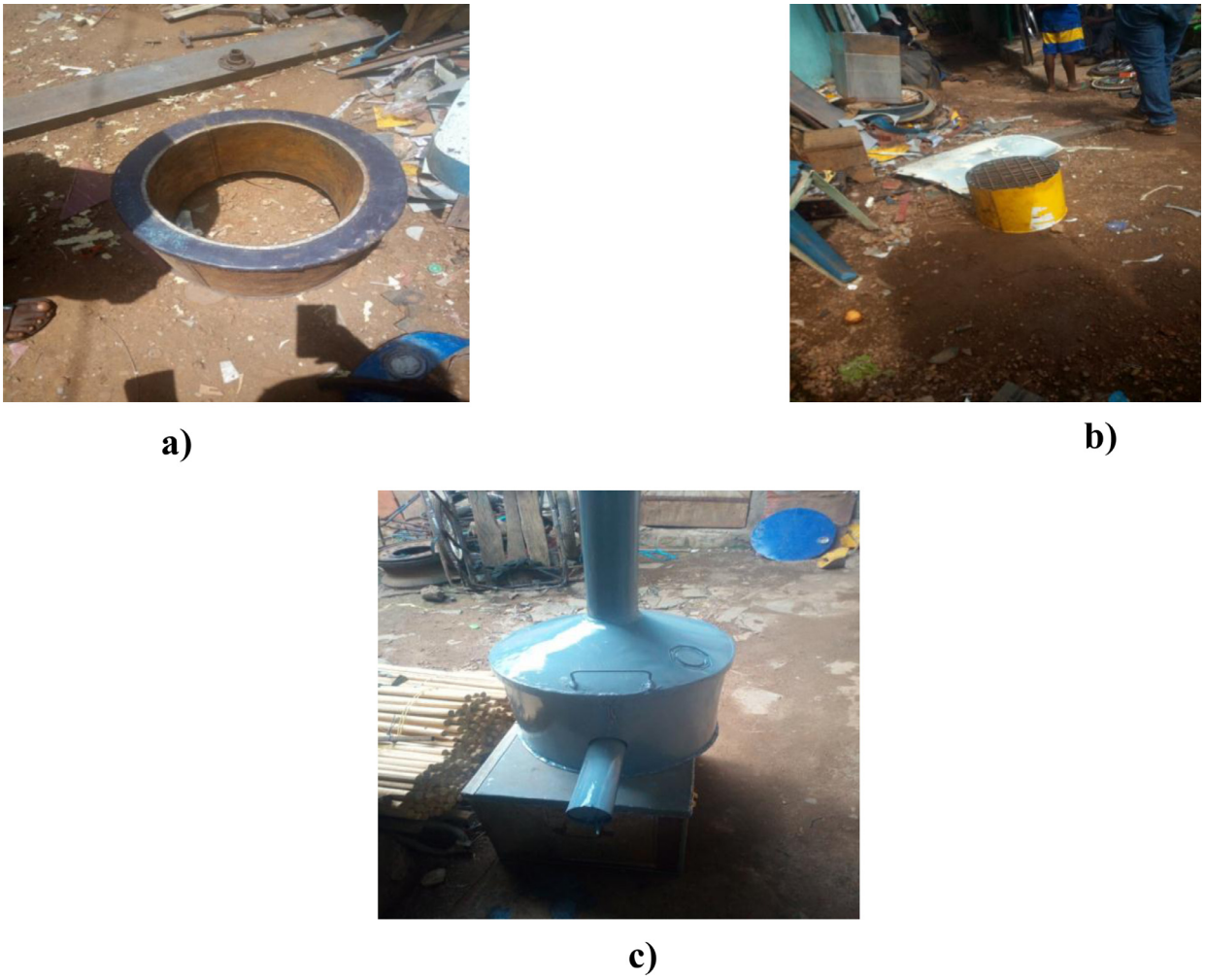


**Fig. 1.** Construction of biochar burning chamber a) inner and outer chambers design b) attachment of rods c) painted complete design.

take place for 20 min (determined from preliminary testing). The temperature variation in the chamber monitored using a thermocouple ranged from 370–400 °C. Biochar can be obtained at temperatures between 350–800 °C [12]. The content of the chamber was continuously checked to ensure it does not burn to ashes. After 20 min, the biochar was then sprinkle with water to prevent further burning with oxygen. The biochar was then collected, sun dried and crushed into fine particles. For discoloration studies the biochar was further washed with distilled water, dried at laboratory temperature (≈30 °C) for seven days and sieved to obtain particles of diameter less than 0.5 mm which were used without further treatment.

*Batch discoloration studies*

The slaughter waste water used was collected at the Djounde abattoir in Maroua (N10° 38. 814′ E014° 20.469′). The water was kept in the laboratory for 24 h to permit sedimentation and was filtered on a Whatman filter paper N° 1. It was then diluted with distilled water to absorbance of 0.054 determined at wavelength of 492 nm (pre-determined) using UV/visible spectrophotometer (spectron23RS, labo med.inc). This value was used as initial concentration for the study of the influence of contact time, pH, temperature and dose of biochar on slaughter house waste water (SHW) discoloration. For the influence of initial concentration, solutions of SHW with absorbances of 0.028, 0.047, 0.053, 0.079 and 0.111 prepared by dilution with distilled water were used. All discoloration experiments were carried out in 250 mL Erlenmeyer flasks with 100 mL of working solution and using 0.05 g of biochar except for study of influence of dose of biochar. All solutions were shaken at 150 rpm for the required time; 0–60 min for the effect of contact time and 15 min for other parameters (obtained equilibrium time) and the flask and its contents kept static in a shade to avoid degradation by sunlight for 24 h. After which 5 mL of SHW solution was decanted and the residual concentration of SHW determined using UV/visible spectrophotometer (spectron23RS, labo med.inc) at 492 nm. The same procedure was used for MB discoloration as well as the same tested parameters. Working MB solutions were prepared from a 1000 mg/L synthetic stock solution prepared by dissolving 1 g of

**Fig. 2.** Biochar production process.

MB (AR grade, $C_{16}H_{18}ClN_3S$, molecular weight = 319.85, $\lambda_{max}$ = 664 nm) in 1 liter of distilled water. While MB initial concentration of 10 mg/L was used to study the influence of other tested parameters, values of 2–20 mg/L were used to study the influence of MB discoloration. All pH adjustments were done using 0.1 M HCl and 0.1 M NaOH. All pH measurements were done using Mettler Toledo Education line pH meter.

The MB or SHW amount discolored (mg/g) was calculated from Eq. (1) while the percentage discoloration (%) was calculated using Eq. (2):

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{1}$$

$$R_e = \frac{(Co\ -\ Ce)}{Co} x\ 100 \tag{2}$$

Where, $C_0$ and $C_e$ (mg/L) are the initial and equilibrium concentrations respectively for MB and initial and equilibrium absorbances for SHW; V (L) is the volume of solution, m (g) is the mass of biochar used; $q_e$ (mg/g) is adsorption capacity and $R_e$ (%) is percentage discoloration.

*Column discoloration studies*

Two Glass columns (for MB and SHW) of 2.5 cm inside diameter and height of 30 cm were used for continuous flow discoloration studies. The column was packed with 7 cm biochar/sand mixture (13.80 g/54.70 g) between two graded levels of sand (5 cm of sand with particles > 250 µm and less than 315 µm from the bottom and 3 cm of large grain size from the top) to avoid loss of adsorbent and also to ensure a closely packed column. Biochar was mixed with sand to improve flow properties and limit clogging of biochar. A series of distilled water filtration were done in the columns prior to adsorption, in order to eliminate air bubbles inside the column. The biochar to sand percentage of 20 was chosen by adapting the study of [18] who obtained optimum filtration results using a 25/75 $Fe^o$/sand mixture. Gravity fed system was used to introduce solutions of BM (10 mg/L, absorbance = 1.753) and SHW (absorbance = 0.757) from the top to the column. Samples were collected from the exit of the column at regular time intervals and analyzed for residual colour. Columns filtration performances were studied by analyzing the shapes of the experimental breakthrough curves (comparing ratio of outlet concentration ($C_t$) to the inlet concentration ($C_o$), ($C_t/C_o$ as a function of time or volume of effluent) obtained by collection of 1000 mL of MB and SHW filtered. The exhaust point is determined when $C_t$ changes to 95% of $C_o$ [24]

## Results and discussion

*Influence of contact time on discoloration*

The discoloration of MB and SHW on biochar was studied from 0–60 min and the results are presented in Fig. 3. The discoloration of both MB and SHW occurred in three phases; very fast in the first five minutes attaining discoloration of 55% for MB and 94% for SHW. This was followed by slowdown and attaining equilibrium in 15 min for the two pollutants (100% discoloration for SHW and 64% for MB). While SHW discoloration showed a steady decrease from 100% at equilibrium to 68% at 60 min, MB discoloration increased slightly from 64% at equilibrium to 68% at 40 min before decreasing again to 65% at 60 min. At the start of the process, biochar has many vacant sites available for reaction. However, as the process proceeds there is a reduction in the number of vacant sites hence a slowdown in discoloration. This slowdown in discoloration is more evident with SHW discoloration than MB. This is due to the fact that SHW has multi constituents such as organic matter, heavy metals, nitrogen, phosphorus, and other typical pollutants [15], which may react or easily block the active sites of the biochar. However, the fact the discoloration of MB and SHW all had similar values at 60 min (68% for SHW and 65% for MB) suggest the maize cob biochar used had a certain fixed number of sites available for reaction. The pH of biochar was determined as 9.01 while that of MB and SHW were 6.19 and 6.09 respectively. It's probably that discoloration was strongly controlled by electrostatic interactions between the negative biochar surface and slightly acidic MB and SHW solutions. This explains why SHW with solution pH of 6.01 had higher discoloration than MB with pH of 6.19.

*Discoloration kinetics and equilibrium isotherms*

While adsorption isotherm helps understand the distribution of pollutant molecules between the solid and liquid phases and in the determination of adsorption capacity and the nature of adsorbate-adsorbent interactions, adsorption kinetics evaluation provides an insight on the rate of adsorption and the rate-limiting step of the transport mechanism, generally used in the modelling and design of the process [19]. The adsorption kinetics and isotherm parameters were determined by fitting the equilibrium adsorption data obtained from the study of the effects of contact time. The isotherm models tested were Langmuir, Freundlich, Dubinin-Radushkevich (D-R) and Temkin while the kinetics models tested were pseudo-first-order, pseudo-second-order and intra-particle diffusion. Equations of these models with their linearized forms and the parameters used in describing discoloration efficiency are all summarized in Table 1 [20,21] while the calculated parameters are presented in Table 2 (kinetic parameters) and Table 3 (isotherm parameters).

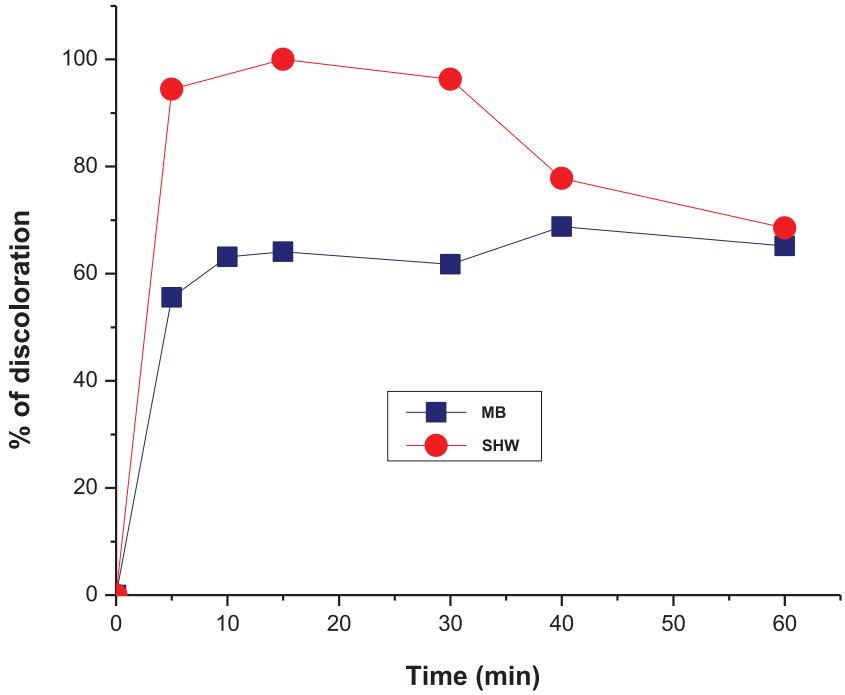


**Fig. 3.** Effect of contact time on MB and SHW adsorption ($C_{o,MB}$ 10 mg/L, $C_{o,SHW}$ 0.054 AB (absorbance); biochar 0.05 g; $pH_{MB}$ 6.19, $pH_{SHW}$ 6.09; temperature 25°C).

**Table 1**
Isotherms and kinetics model equations [20,21].

| Model | Main equation | Linear form | Characteristic/derived parameters |
|---|---|---|---|
| **Isotherm Models** | | | |
| **Langmuir** | $\frac{q_e}{q_m} = \frac{K_L C_e}{1+bC_e}$ | $\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m}$ | $q_m$ = maximum monolayer adsorption capacity (mg/g)<br>$b$ = Langmuir equilibrium constant (L/mg)<br>$R_L = \frac{1}{1+bC_0}$ = separation factor, indicator of favourability of adsorption |
| **Freundlich** | $q_e = K_F(C_e)^{1/n}$ | $lnq_e = lnK_F + \frac{1}{n}lnC_e$ | $K_F$ = Freundlich maximum adsorption capacity (mg/g)(L/mg)$^{1/n}$<br>$n$ = measures adsorption intensity (dimensionless) |
| **Dubinin-Radushkevich *(D-R)*** | $q_e = X_m exp(-K\varepsilon^2)$ | $lnq_e = lnX_m - K\varepsilon^2$ | $X_m$ = adsorption capacity (mg/g)<br>$K$ = constant related to the adsorption energy (mol$^2$/kJ$^2$)<br>$E = 1\sqrt{2\ K}$ = adsorption energy(kJ/mol) |
| **Temkin** | $q_e = BlnA_T.C_e$ | $q_e = BlnA_T + BlnC_e$ | $A_T$: equilibrium binding constant (L/mg)<br>$b_T = \frac{RT}{B}$ = adsorption energy (kJ/mol) |
| **Kinetic models** | | | |
| **Pseudo-first-order** | $\frac{dq(t)}{dt} = k_1(q_{eq} - q_t)$ | $\ln(q_e - q_t) = \ln q_e - k_1 t$ | $K_1$ = pseudo-first-order rate constant (min$^{-1}$) |
| **Peudo-second-order** | $\frac{dq(t)}{dt} = k_2(q_{eq} - q_t)^2$ | $\frac{t}{q_t} = \frac{1}{k_2 q_e{}^2} + \frac{t}{q_e}$ | $k_2$ =Peudo-second-order rate constant (g/mg/min)<br>$h = k_2 qe^2$ = initial adsorption rate (mg/g·min)<br>$t_{1/2} = \frac{1}{k_2 q_e{}^2}$ = half adsorption time (min) |
| **Intra-particle diffusion** | $q_t = k_{id}t^{1/2}$ | $q_t = k_{id}t^{1/2} + C$ | $k_{id}$ = intra-particle diffusion rate constant (mg/g min$^{1/2}$) |

**Table 2**
Maize cob biochar kinetic parameters for the discoloration of MB and SHW.

| | Pseudo-first-order | | | | Pseudo-second-order | | | | | | Intra-particle diffusion | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $k_1$ | $q_{e,C}$ | $q_{e,ex}$ | $R^2$ | $k_2$ | $q_{e,C}$ | $q_{e,ex}$ | $R^2$ | h | $t_{1/2}$ | $k_{id}$ | C | $q_{e,ex}$ | $R^2$ |
| **MB** | 0.024 | 0.778 | 12.82 | 0.087 | 0.096 | 13.33 | 12.82 | 0.997 | 17.065 | 0.059 | 0.298 | 11.189 | 12.82 | 0.497 |
| **SHW** | 0.036 | 0.004 | 0.108 | 0.609 | 3.065 | 0.072 | 0.108 | 0.978 | 0.015 | 65.338 | 0.006 | 0.123 | 0.108 | 0.654 |

Units of parameters: $k_1$ = min; $q_{e,C} = q_{e,ex}$ = C = mg/g & AB/g; $k_2$ = g/mg/min & g/AB/min; h = mg/g·min & AB/g·min; $t_{1/2}$ = min; $k_{id}$ = mg/g/min$^{1/2}$ (AB/g/min$^{1/2}$).
Units of concentration: MB = mg/L and SHW = AB (absorbance).
$q_{e,C}$ and $q_{e,ex}$ are respectively, calculated and experimental equilibrium amounts adsorbed.

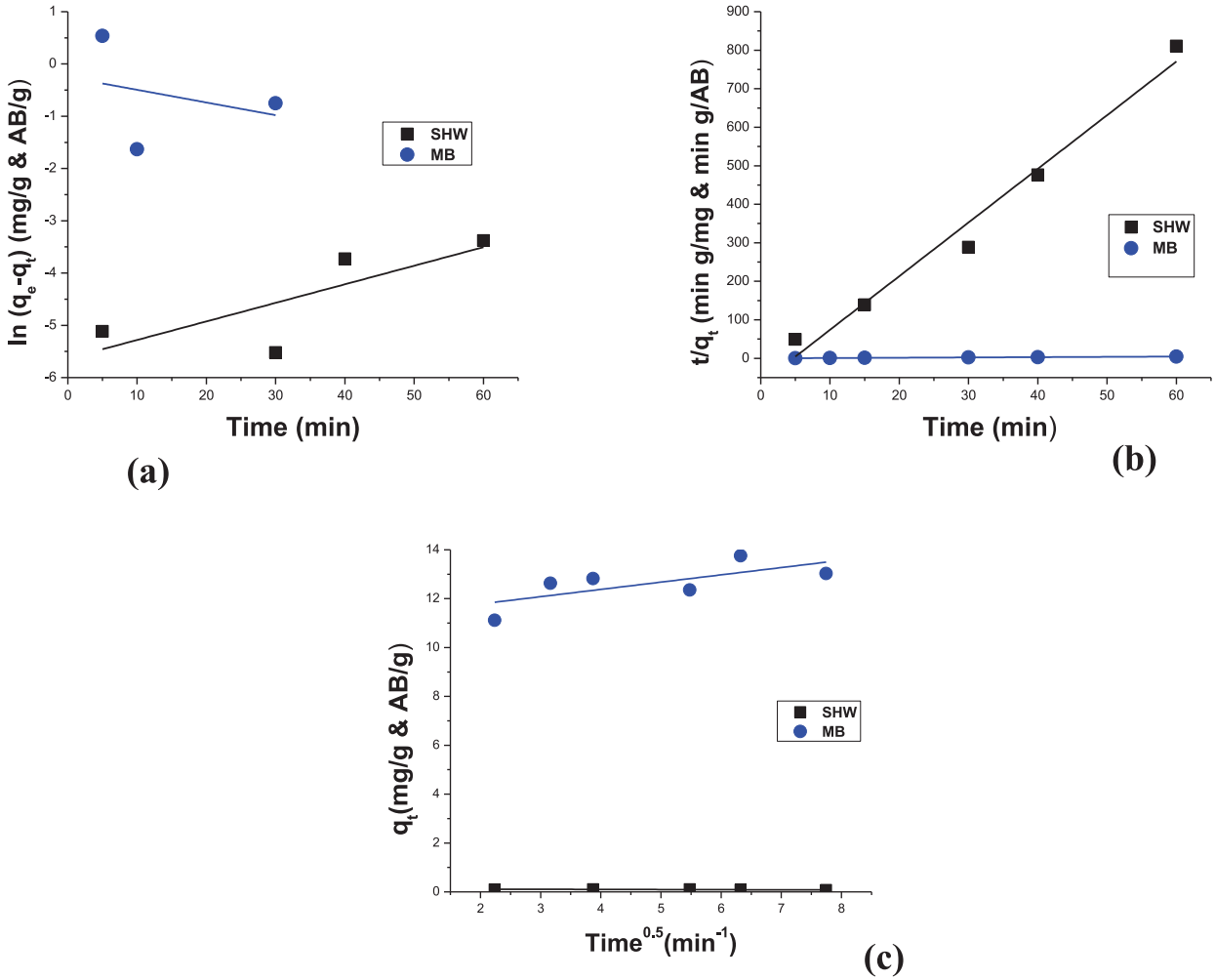


**Fig. 4.** Linearized form plots of (a) Pseudo-first order b) Pseudo-second order and c) Intra-particle diffusion kinetic models.

The linearized plots of Pseudo-first order model for SHW and MB discoloration are shown in Fig. 4a. From these plots and calculated parameters in Table 2, it is observed that this model does not describe the discoloration of SHW and MB on maize cob biochar as they all have very low correlation coefficients and the calculated and equilibrium amounts discoloured are so different.

Equally, the intra-particle diffusion model (Fig. 4c), also showed least fit for SHW and MB removal on maize cob biochar with very low correlation coefficients (Table 2).

For the Pseudo-second order model, the initial adsorption rate ($h$), the equilibrium adsorption capacity ($q_e$), and the second-order constant ($k_2$) were determined experimentally from the slope and intercept of plot t/qt versus t, Fig. 4b and values of the parameters are presented in Table 2. It can be seen from Table 2 that the correlation coefficients for MB and SHW discoloration using maize cob biochar are 0.997 and 0.978 respectively indicating a good fit of this model. This good fit is further supported by the strong correlation between experimental and calculated equilibrium amounts adsorbed for both SHW and MB. SHW has a higher rate of discoloration ($k_2 = 3.065$ g/mg/min) than MB ($k_2 = 0.096$ g/mg/min), Table 2. However, the reverse is observed for initial discoloration rate, h with MB having a higher initial discoloration rate (17.065 mg/g·min) than SHW (0.015 (mg/g·min).

The half discoloration time $t_{1/2}$ (Table 1) is the time required for biochar to discolor half the amount discolored at equilibrium. From Table 2, MB and SHW have $t_{1/2}$ values of 0.059 min and 65.338 min respectively indicating faster discoloration rate of MB than SHW and corroborating h values results.

Other studies have also shown that Pseudo-second order kinetic model best describe MB discoloration on Biochar [22,23].

The linearized plots of Langmuir, Freundlich, Dubinin-Radushkevich (D-R) and Temkin isotherms are shown in Fig. 5a, b, c and d respectively and their calculated parameters presented in Table 3. It is seen from Table 3 that Langmuir, Freundlich Dubinin-Radushkevich and Temkin isotherm models describe the discoloration of MB on tested maize cob biochar

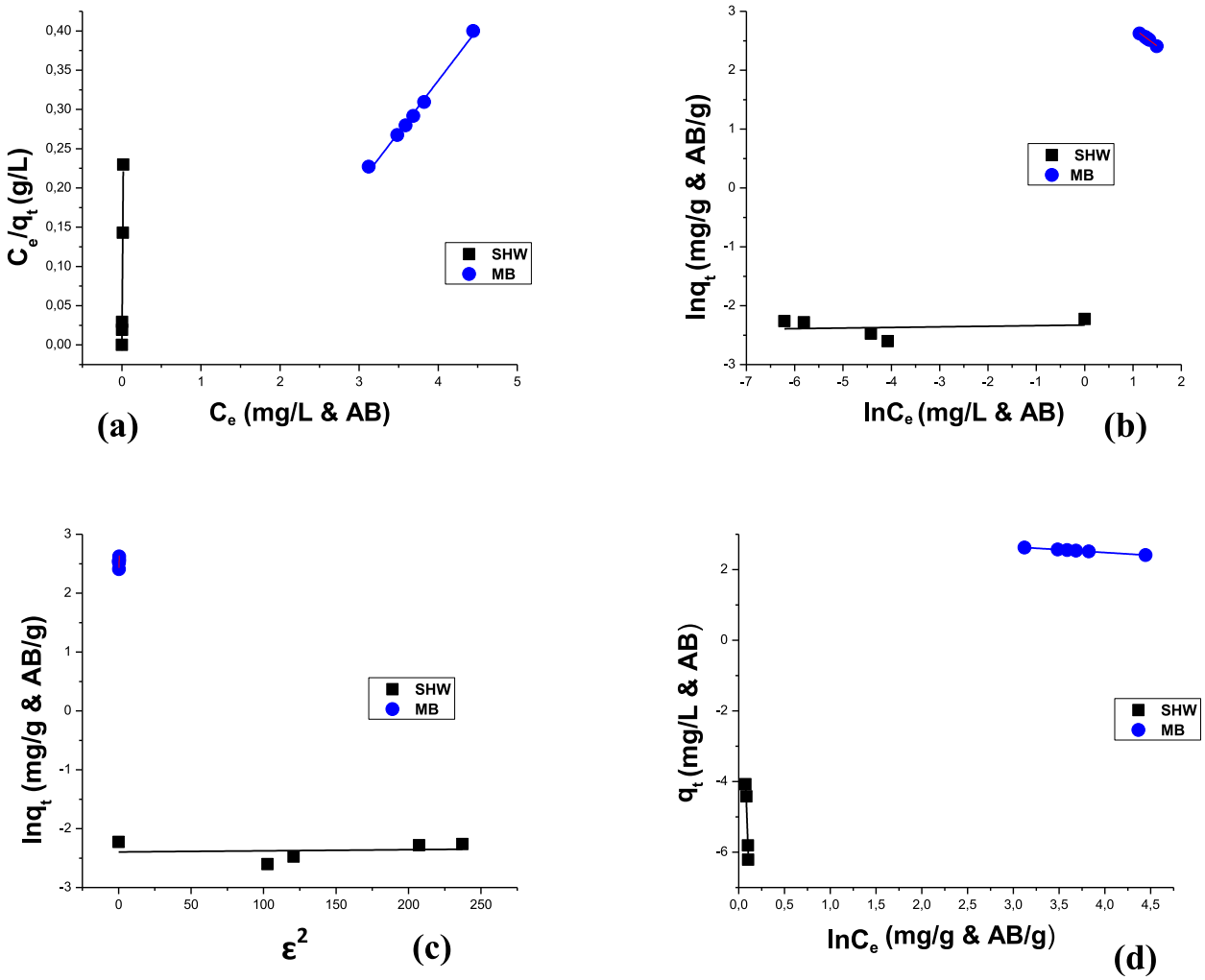


**Fig. 5.** Linearized form plots of a) Langmuir, b) Freundlich, c) Dubinin Radushkevich and d) Temkin isotherms.

**Table 3**
Maize cob biochar isotherm parameters for the discoloration of MB and SHW.

| | Langmuir | | | | Freundlich | | | Dubinin-Radushkevich | | | | Temkin | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $q_m$ | b | $R^2$ | $R_L$ | $K_F$ | n | $R^2$ | $X_m$ | K | E | $R^2$ | B | $A_T$ | $b_T$ | $R^2$ |
| **MB** | 7.58 | 0.69 | 0.995 | 0.13 | 27.782 | 1.643 | 0.990 | 8.898 | 0.9583 | 0.722 | 0.955 | −0.16 | $4.1 \times 10^{-9}$ | −15.28 | 0.999 |
| **SHW** | 0.075 | 1916.71 | 0.993 | 5.2E-05 | 0.097 | 9.010 | 0.024 | 0.091 | 0.0002 | 50 | 0.012 | −70.80 | 0.98 | −0.04 | 0.968 |

Units of parameters: $q_m = X_m =$ mg/g & AB/g; $b = b_T = L$/mg & L/AB; $K_F = (mg/g)(L/mg)^{1/n}$ & $(AB/g)(L/AB)^{1/n}$; $K = mol^2/KJ^2$; $E = b_T =$ kJ/mol.

with correlation coefficients ranging from 0.955–0.999 but only Langmuir and Temkin isotherm models describe the discoloration of SHW with correlation coefficients ranging from 0.968 in Temkin to 0.993 for Langmuir. While Temkin best fit MB discoloration data ($R^2 = 0.999$), Langmuir best describe SHW discoloration ($R^2 = 0.993$).

The Freundlich model describes multilayer discoloration process which takes place on heterogeneous surface [19,21]. Values of *n* in the range 2–10 represent good, 1–2 moderately difficult, and less than 1 a poor adsorptive potential [24]. Freundlich model therefore described moderately difficult MB discoloration on maize cob biochar with n value of 1.643.

The Dubinin-Radushkevich isotherm assumes a heterogeneous surface. The significance of applying Dubinin-Radushkevich model is to determine apparent adsorption energy, *E* (kJ/mol) (Table 1). If the value of E is between 8 and 16 kJ/mol, ion exchange is the main sorption process in the system. If the value is lower than 8 kJ/mol, physical sorption is the main sorption mechanism and if the value is greater than 16 kJ/mol, it may be chemisorption [19,21]. D-R represented a good fit for MB discoloration with discoloration energy of 0.722 kJ/mol, showing that the process was physical.

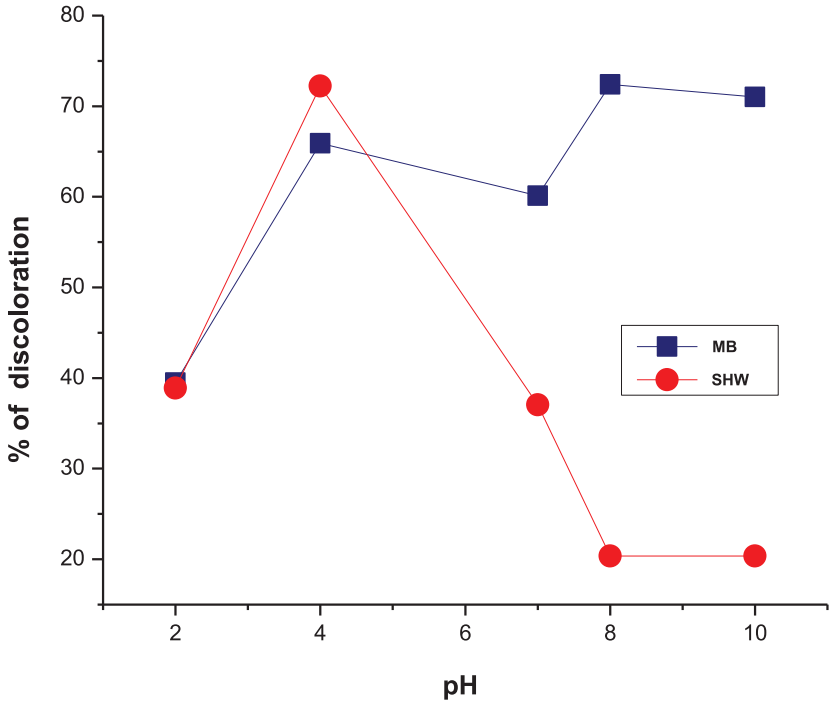


**Fig. 6.** Effect of solution pH on MB and SHW adsorption ($C_{o,MB}$ 10 mg/L, $C_{o,SHW}$ 0.054 AB (absorbance); biochar 0.05 g; temperature 25°C).

Temkin model assumes that the heat of adsorption of the adsorbates in the layer decreases linearly rather than logarithmically with coverage due to adsorbent-adsorbate interactions [20,25]. The Temkin isotherm mode described MB and SHW discoloration with Temkin constant, $b_T$ (linked to the heat of discoloration) values of −15.28 and −0.04 kJ/mol for MB and SHW respectively, showing physisorption mechanism controlled MB and SHW discoloration on tested biochar [19,21].

The Langmuir isotherm is meant for monolayer discoloration taking place over an even homogeneous adsorbent surface. Separation factor, $R_L$, (Table 1) is considered as a more reliable indicator of the discoloration. For favorable discoloration, $0 < R_L < 1$; while $R_L > 1$, $R_L = 1$ and $R_L = 0$, respectively, describe unfavorable, linear and irreversible discoloration [19,21]. Langmuir isotherm model described both MB and SHW discoloration with monolayer capacities of 7.58 and 0.075 mg/g (Table 3) respectively showing affinity of MB and SHW for maize cob biochar surface. This affinity is more for SHW than MB as evident from the Langmuir equilibrium constant, b (1916.71 L/mg for SHW and 0.69 L/mg for MB) and the Temkin equilibrium constant $A_T$ (0.98 L/mg for SHW and $4.1 \times 10^{-9}$ L/mg for MB) (Table 3). This trend is further supported by very low $R_L$ value of $5.2 \times 10^{-5}$ for SHW against 0.13 for MB. These results do show that slaughter house waste water is easily discolored than methylene blue using maize cob biochar in batch process. While MB discoloration involves homogenous and heterogeneous sites (Langmuir, Freundlich, D-R and Temkin fit), SHW involves homogenous sites (Langmuir and Temkin fit).

*Influence of pH*

The study of influence of pH on discoloration of MB and SHW is important because a change in pH can lead to ionization of the pollutant molecules as well as adsorbent surface functional groups. The pH was varied from 2–10, using 0.05 g biochar at 25 °C, 10 mg/L MB initial concentration and absorbance of 0.054 for SHW. Results are shown in Fig. 6, where it is observed that SHW discoloration is favourable at acidic pH (maximum at pH of 4) while MB adsorption is more favourable in the basic pH (maximum at pH of 8). MB is a cationic dye, so its high discoloration at basic pH is due to attractions between the positive charge of MB and protonated negative charges of functional groups on biochar. Similar trends with favourable MB discoloration on biochar at basic pH have been reported by other authors [22,26]. According to [27], the nature of colour in biological wastewater is often organic and caused by humic matter which is basic in structure. Thus, this probably accounts for SHW favourable discoloration at acidic pH resulting from the negative charges of the humic matter content of SHW and positively protonated functional groups of biochar at acidic conditions.

*Influence of biochar dosage*

The effect of dose of biochar on SHW and MB discoloration was studied for 0.03–0.15 g biochar at solution pH, 25 °C, 10 mg/L MB and SHW absorbance of 0.054. The results presented in Fig. 7 shows that the efficiency of MB discoloration

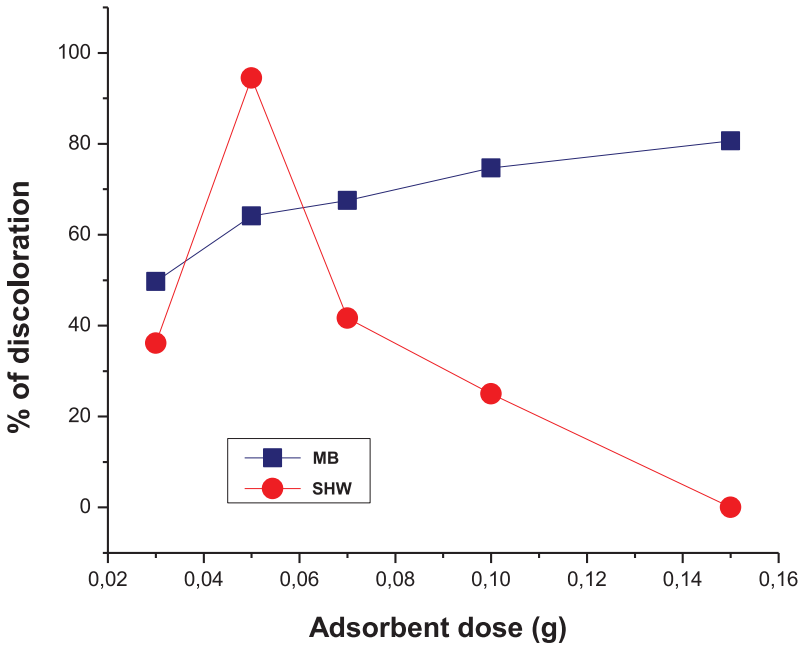


**Fig. 7.** Effect of biochar quantity on MB and SHW adsorption ($C_{o,\ MB}$ 10 mg/L, $C_{o,SHW}$ 0.054 AB (absorbance); $pH_{MB}$ 6.19, $pH_{SHW}$ 6.09; temperature 25°C).

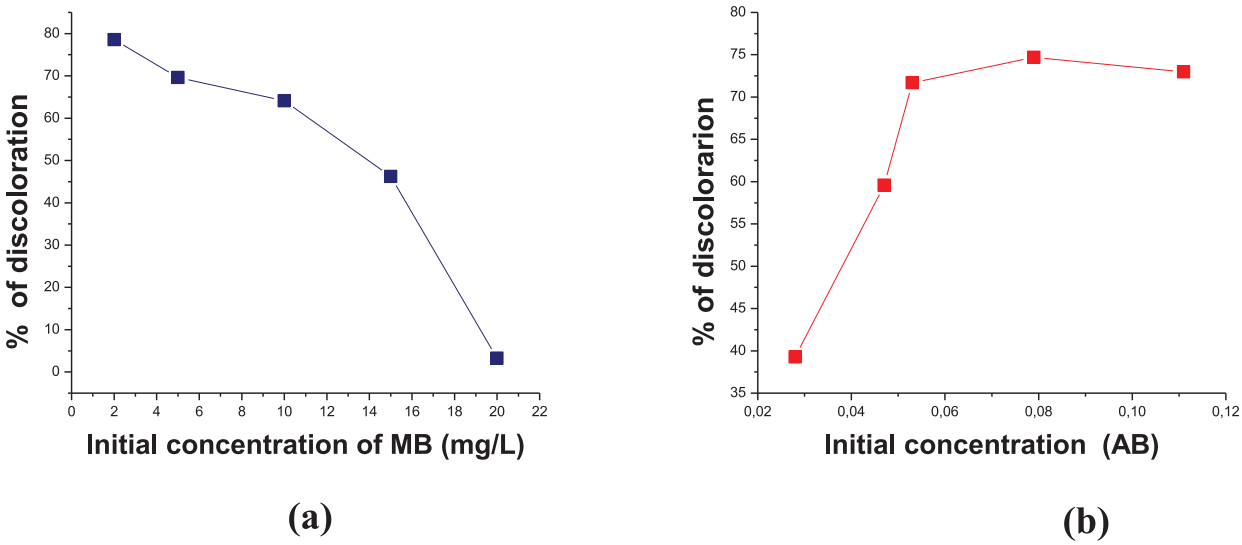


**Fig. 8.** Effect of a) MB and b) SHW initial concentrations on adsorption by biochar. (biochar 0.05 g; $pH_{MB}$, 6.19 $pH_{SHW}$ 6.09; temperature 25°C).

increases with increase in the amount of biochar while SHW discoloration increased to 0.05 g and decreases to 0% discoloration at 0.15 g of biochar. Increase in discoloration with increase in mass of biochar is due to increase in surface area and hence the number of active sites [23]. However, the decrease in discoloration with increase in the mass of biochar may be due to particle aggregation which may lead to a decrease in total surface area of the biochar and an increase in diffusional path length [26]. Equally, 0% discoloration of SHW at 0.15 g biochar may be due to strong repulsion between the basic humic matter dominated SHW and negatively charged biochar surface.

*Influence of MB and SHW initial concentrations*

The effect of MB and SHW initial concentrations on their discoloration efficiency by maize cob biochar is displayed in Fig. 8a and b respectively. This result shows that MB discoloration (Fig. 8a) decreases with increase initial concentration while SHW discoloration (Fig. 8b) increases with increase initial concentration. Limitation of active sites with increase of initial MB concentration may be responsible for the decrease in discoloration [23] who also reported similar results for MB

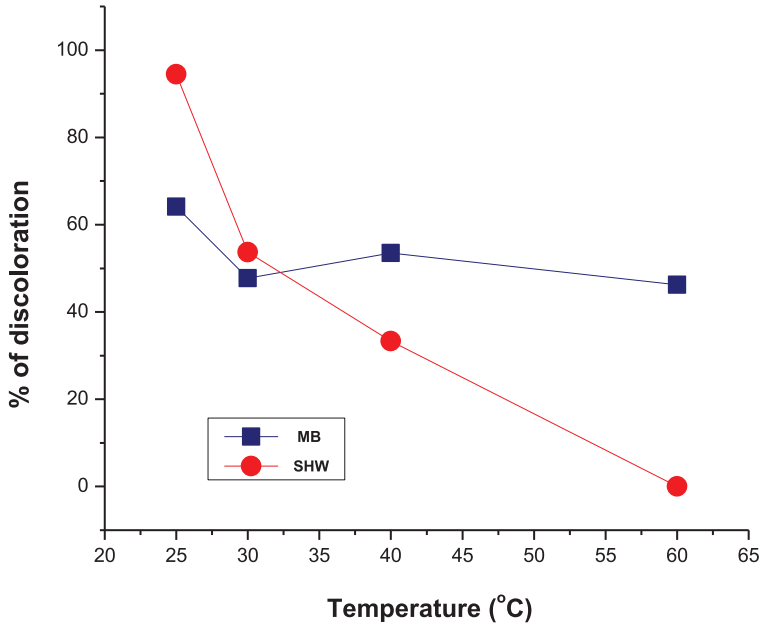


**Fig. 9.** Effect of solution temperature on MB and SHW adsorption ($C_{o,MB}$ 10 mg/L, $C_{o\ SHW}$ 0.054 AB(absorbance); biochar 0.05g; $pH_{MB}$ 6.19, $pH_{SHW}$ 6.09).

removal on biochar. Meanwhile, increase in discoloration of SHW with increase in SHW initial concentration result from an important driving force provided at higher initial concentration necessary to overcome all mass transfer resistance [22,28]. This opposite behavior of SHW and MB also shows that their composition is very different with constituents of different molecular sizes.

*Thermodynamic study*

Thermodynamic studies are necessary do determine if the discoloration process is spontaneous, exothermic or endothermic. To accomplish this, thermodynamic parameters such enthalpy $\Delta H^0$, entropy $\Delta S^0$, and Gibbs free energy $\Delta G^0$ can be obtained from the following equations:

$$\Delta G^0 = -RTK \tag{3}$$

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{4}$$

Where $R$ is the ideal gas constant (kJ/mol/K) and $T$ is the temperature (K). The enthalpy change ($\Delta H$) and the entropy change ($\Delta S$) are calculated from a plot of lnK versus 1/T.

K was calculated from $K = C_{ads}/C_e$ (5); $C_{ads} = C_o - C_e$

Where K is the equilibrium constant, $C_e$ is the residual concentration (mg/L) at temperature T, $C_o$ is the initial concentration (mg/L) (residual and initial absorbances for SHW), $C_{ads}$ is the concentration of adsorbate in the adsorbent at equilibrium (mg/L) at temperature T.

The influence of temperature was studied from 25–60 °C and the results are shown in Fig. 9. As seen from Fig. 9, SHW and MB discoloration on maize cob biochar decreases with increase in temperature and attaining 0% discoloration for SHW at 60 °C. The decrease may be due to destruction of the active sites of the biochar with increasing temperature and hence a reduction in surface area of biochar available for reaction. Equally, the decrease may be due to the increase in MB and SHW molecules solubility with increase in temperature, which hinders their discoloration because they would have more affinity with the solvent than with the adsorbent. Also, increase in temperature caused an increase in the agitation of the dissolved chemical species, reducing its interaction with the adsorbent, hence a decreased in the force of the attraction between the SHW and adsorbent. The two later explanations were surely more pronounced with SHW than with MB accounting for its 0% discoloration at 60 °C.

The calculated thermodynamic parameters are summarized in Table 4. The Gibbs free energy turns positive with increase in temperature for SHW and MB indicating that the discoloration process is not spontaneous with increasing temperature. The negative value of $\Delta H°$ for SHW and MB discoloration shows that the adsorption is an exothermic process. Thus, increase in temperature would decrease discoloration efficiency. Moreover, the entropy change of the process is negative, indicating a decreased randomness at the solid-solution interface thus a difficult discoloration. These results are consistent with those obtained with isotherm study (Fig. 7).

**Table 4**
Maize cob biochar thermodynamic parameters for the discoloration of MB and SHW.

| | $C_0$ | Temperature (K) | Equilibrium constant | ΔG° (KJ/mol) | ΔH° (KJ/mol) | ΔS° (KJ/mol K) |
|---|---|---|---|---|---|---|
| MB | $C_0 = 10$ (mg/L) | 298 | 1.79 | −1.44 | −11.908 | **−0.037** |
| | | 303 | 0.91 | 0.23 | | |
| | | 313 | 1.15 | −0.36 | | |
| | | 333 | 0,86 | 0.41 | | |
| SHW | $C_0 = 0{,}054$ (AB) | 298 | 17.00 | −7.02 | **−49,221** | −0.153 |
| | | 303 | 1.16 | −0.37 | | |
| | | 313 | 0.50 | 1.80 | | |
| | | 333 | 0.00 | 0.00 | | |

$C_0$ = initial concentration AB = Absorbance.

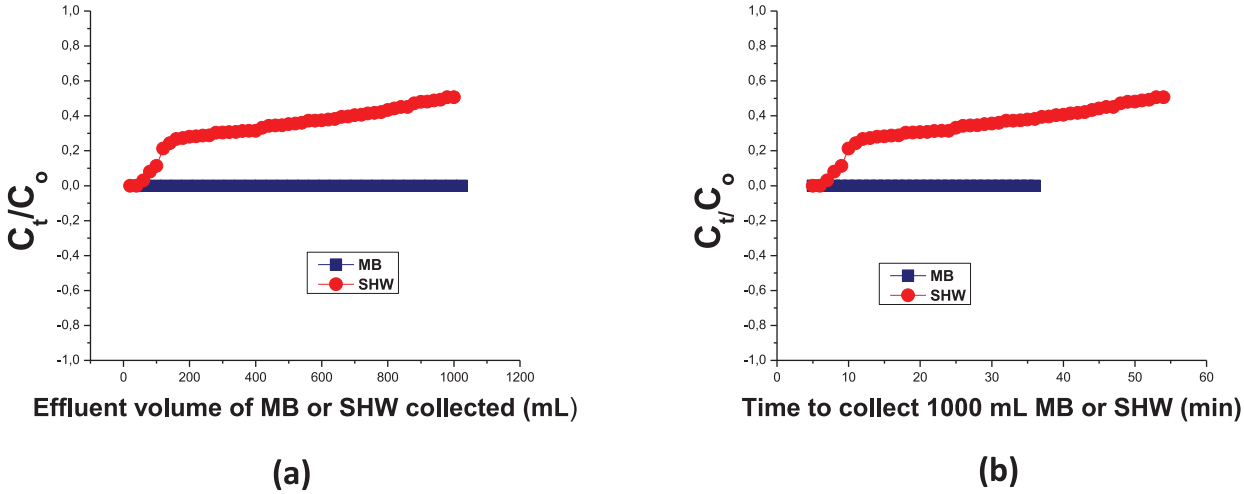


**Fig. 10.** Breakthrough curves of MB and SHW column removal on biochar/sand reactive zone a) function of volume of effluent b) function of flow time.

*Column filtration*

Filtration has been identified as the simplest efficient technology [29] especially for local communities and homes with no electricity in developing countries. The main interest of this analysis is that these results should help in the design of a good stand-alone filter demanding neither electricity nor addition of chemicals and using local available materials as way of resolving persistent water quality linked epidemics in developing countries. These results are presented in Fig. 10a and b. From Fig. 10a, it can be seen that all 1000 mL of MB continuously filtered was completely discoloured and this took just 36 min, Fig. 10b. Meanwhile all 1000 mL of SHW was continuously filtered in 54 min (Fig. 10b) with a breakthrough time of eight minutes or colour was completely removed up to eight minutes (Fig. 10a and b). The high discoloration obtained with cationic MB may be due to increase in the number of active sites resulting from the addition of sand with a negative surface. Sand mixed with other materials has been shown to enhance the discoloration of MB [17,30]. The designed system can discolor SHW although only for 8 min and this may be due to the electrostatic repulsion of negatively charged column (packed with negatively charged biochar and sand) and basic humic matter content of SHW. However, the materials are highly available and hence low cost meaning they will provide a comparable removal capacity per unit cost for large scale or series filtration designs.

## Conclusion

In this study, batch and continuous filtration systems were used to carry out a comparative study to investigate the effectiveness of discoloration of methylene blue and slaughter house waste water using maize cobs biochar produced by a system constructed in the laboratory. At equilibrium time of 15 min, SHW is 100% discoloured against 64% for MB. SHW discoloration is favourable at acidic pH while MB adsorption is more favourable in the basic pH. MB discoloration increases with increase in the amount of biochar while SHW discoloration increased to 0.05 g, then decreasing to 0% with increasing biochar. Conversely, MB discoloration decreases with increase initial concentration while SHW discoloration increases with increase initial concentration. Both SHW and MB discoloration decreases with increase in temperature attaining 0% for SHW at 60 °C. Pseudo-second order kinetic model best describe the discoloration of MB and SHW. Langmuir, Freundlich Dubinin-Radushkevich and Temkin isotherm models describe the discoloration of MB but only Langmuir and Temkin isotherm models

describe the discoloration of SHW. Slaughter house waste water is easily discolored than methylene blue using maize cob biochar in batch process as evident from calculated Langmuir and Temkin equilibrium constants, Langmuir monolayer capacity and Langmuir separation factor ($R_L$). The discoloration process is exothermic and less spontaneous with increasing temperature. A biochar/sand mixture filtration is more efficient in discoloring MB with than SHW. Maize cob biochar can be effectively be used to remove colour from methylene blue containing waste water and slaughter house waste water in an inexpensive process.

## Conflict of interest

No competing interests exist between the authors.

## Acknowledgements

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

## References

[1] S.N. Jain, P.R. Gogate, NaOH-treated dead leaves of Ficus racemosa as an efficient biosorbent for Acid Blue 25 removal, Int. J. Environ. Sci. Technol. 14 (2017) 531–542.
[2] Z. Aksu, A.I. Tatli, O. Tunc, A comparative adsorption/ biosorption study of Acid Blue 161: effect of temperature on equilibrium and kinetic parameters, Chem. Eng. J. 142 (2008) 23–39.
[3] C. Bustillo-Lecompte, M. Mehrvar, Slaughterhouse wastewater: Treatment, management and resource, recovery. (2017) http://dx.doi.org/10.5772/65499.
[4] S.P. Buthelezi, A.O. Olaniran, B. Pillay, Textile dye removal from wastewater effluents using bioflocculants produced by indigenous bacterial isolates, Molecules 17 (2012) 14260–14274.
[5] M. Saeed, A. Haq, M. Muneer, et al., Degradation of direct black 38 dye catalyzed by lab prepared nickel hydroxide in aqueous medium, Glob. Nest. 18 (2016) 309–320.
[6] R.B. Afnabi, R.P. Nameni, S.S. kamdem, V.N. Ngwa, J.J.E. Ngang, Typology of the cameroon traditional slaughterhouses based on hygiene practices, Adv. Anim. Vet. Sci. 2 (2014) 477–487 2014.
[7] J. Gongwala, S.A. Djepang, P. Abba, G. Payom, S. Laminsi, D. Njopwouo, Treatment of wastewater from a slaughterhouse by gliding arc humid air plasma: chlorophyll degradation, Int. J. Environ. Protect. Policy 2 (2014) 118–125.
[8] N. Gatcha-Bandjun, Evaluation du potentiel des filtres à base de fer métallique pour l'approvisionnement en eau et la salubrité urbaine: cas de la ville de Maroua (Cameroun), in: Approvisionnement en eau potable en Afrique, Une technologie appropriée pour relever le défi, Africa & Science, 2016, pp. 37–50.
[9] P.S. Kumar, S. Ramalingam, C. Senthamarai, et al., Adsorption of dye from aqueous solution by cashew nut shell: studies on equilibrium isotherm, kinetics and thermodynamics of interactions, Desalination 261 (2010) 52–60.
[10] M. Saeed, S. Adeel, M. MIlyas, et al., Oxidative degradation of methyl orange catalyzed by lab prepared nickel hydroxide in aqueous medium, Desalin. Water Treat. 57 (2015) 1–10 a.
[11] V.K. Gupta, P.J.M. Carrott, M.M.L. Ribeiro Carrott, Suhas, low-cost adsorbents: growing approach to wastewater treatment—a review, Criti. Rev. Environ. Sci. Technol. 39 (2009) 783–842.
[12] M.T. Amin, A.A. Alazba, M. Shafiq, removal of copper and lead using banana biochar in batch adsorption systems: isotherms and kinetic, Studies Arab J. Sci. Eng. 43 (2018) 5711–5722.
[13] J. Tang, W. Zhu, R. Kookana, A. Katayama, Characteristics of biochar and its application in remediation of contaminated soil, J. Biosci. Bioeng. 116 (2013) 653–659.
[14] J.M. Patra, S.S. Panda, N.K. Dhal, Biochar as a low-cost adsorbent for heavy metal removal: a review, Int. J. Res. Biosci. 6 (2017) 1–7.
[15] Y. Deng, T. Zhang, Q. Wang, Biochar Adsorption treatment for typical pollutants removal in livestock wastewater: a review, Book: Engineering Applications of Biochar, 2017 http://dx.doi.org/10.5772/intechopen.68253.
[16] I. Samomssa, N.Y. Jiokap, R. Kamga, Energy potential of waste derived from some food crop products in the northern part of cameroon, Int. J. Energy Power Eng. 4 (2015) 342–352.
[17] C. Tsamo, J. Atchana, P.N.D. Djonga, Testing the suitability of red mud based systems as permeable reactive barrier (PRB) materials, J. Chem. Appl. Chem. Eng. 2 (2018) 1–6.
[18] B.D. Btatkeu-K, H. Olvera-Vargas, J.B. Tchatchueng, C. Noubactep, S. Caré, Determining the optimum $Fe^0$ ratio for sustainable granular $Fe^0$/sand water filters, Chem. Eng. J. 247 (2014) 265–274.
[19] P.D. Djantio, C. Tsamo, M.R.S. Topet, F.T. Matsinkou, B.B. Loura, Utilisation of waste from the production of millet derived local drink as adsorbent for phosphate removal from aqueous solution, Ind. Chem. Eng. (2019), doi:10.1080/00194506.2019.1569562.
[20] O.V. Shikuku, R. Zanella, C.O. Kowenje, F.F. Donato, N.M.G. Bandeira, O.D. Prestes, Single and binary adsorption of sulfonamide antibiotics onto iron–modifed clay: linear and nonlinear isotherms, kinetics, thermodynamics, and mechanistic studies, Appl. Water Sci. 8 (2018) 1–12.
[21] C. Tsamo, D.J.H. Tchouanyo, D. Meali, Treatment of red mud with distilled water to improve its efficiency to remove methylene blue from aqueous solution, Int. Res. J. Pure Appl. Chem. 15 (2017) 1–19.
[22] Y. Xu, Y. Liu, S. Liu, X. Tan, G. Zeng, W. Zeng, Y. Ding, W. Cao, B. Zheng, Enhanced adsorption of methylene blue by citric acid modification of biochar derived from water hyacinth (Eichornia crassipes), Environ. Sci. Pollut. Res. doi: 10.1007/s11356-016-7572-6.
[23] M. Mupa, D.D. Rutsito, C. Musekiwa, Removal of methylene blue from aqueous solutions using biochar prepared from *Eichhorrnia crassipes* (Water Hyacinth)-molasses composite: kinetic and equilibrium studies, Afr. J. Pure Appl. Chem. 10 (2016) 63–72.
[24] C. Tsamo, I. Bachirou1, I. Samomssa, T.B. Fouogoung, Removal of hexavalent chromium from aqueous solution using unmodified saw dust: batch and column studies, Curr. J. Appl. Sci. Technol. 32 (2019) 1–16.
[25] V.O. Shikuku, C.O. Kowenje, F.O. Kengara, Errors in parameters estimation using linearized adsorption isotherms: sulfadimethoxine adsorption onto kaolinite clay, Chem. Sci. Int. J. 23 (2018) 1–6.
[26] G. Yang, L. Wu, Q. Xian, F. Shen, J. Wu, Y. Zhang, Removal of congo red and methylene blue from aqueous solutions by vermicompost derived biochars, PLos ONE 11 (2016) 1–18, doi:10.1371/journal.pone.0154562.
[27] J.M. Semmens, T.K. Field, Coagulation: experiences in organics removal, J. Am. Water Works Assoc. 72 (1980) 476–483.
[28] W.A.W.AbK Ghania, A. Mohd, D.K. Mahmoud, N.Z. Rebitanim, L. Sanyang, R.B. Zainudin, Adsorption of methylene blue on sawdust-derived biochar and its adsorption isotherms, J. Purity Utility React. Environ. 2 (2013) 34–50.
[29] M. Lea, Biological Sand Filters: low-Cost bioremediation technique for production of clean drinking water, Curr. Prot. Microbiol. (2008) 1G.1.1–1G.1.28, doi:10.1002/9780471729259.mc01g01s9.
[30] G. Mitchell, P. Poole, H.D. Segrove, Adsorption of methylene blue by high-silica sands, Nature 176 (1955) 1025–1026.