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Heavy metal ions adsorption from dairy industrial wastewater using activated carbon from milk bush kernel shell

Tinuade J. Afolabi, Abass O. Alade*, Monsurat O. Jimoh, Isaiah O. Fashola

Faculty of Engineering, Department of Chemical Engineering, Ladoke Akintola University of Technology, P.M.B. 4000, Ogbomosho, Nigeria, Tel. +234 8036669764; email: tinuadeafolabi@yahoo.com (T.J. Afolabi), Tel. +234 703885961; email: abasslad@yahoo.com (A.O. Abass), Tel. +234 7065790838; email: jimonseur2013@gmail.com (M.O. Jimoh), Tel. +234 8027301591; email: fashola_israel@yahoo.com (I.O. Fashola)

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ABSTRACT

Activated carbons (MBK400 and MBK600), produced from milk bush kernel shells, were carbonized at 400 and 600˚C, respectively, activated with H_3PO_4, and subsequently, employed to remove heavy metals (cadmium, lead, nickel, zinc, iron, and copper) in dairy industrial wastewater (DIWW). Effects of doses (1.0–3.0 g/L) and contact time (5–25 min) at constant agitation (120 rpm) on removal efficiencies and adsorption capacities of the agricultural precursors were investigated. Four types of Langmuir isotherm model were used to fit the adsorption of the heavy metals. The pH of the treated DIWW increased from 6.1 to a range of 6.7–6.9 and 6.8–6.9 with MBK400 and MBK600, respectively, while, there were slight increase in the conductivity of the treated DIWW, except with 3.0 g of MBK400, which reduced the conductivity from 377 to 345 μS/cm. The maximum percentage of cadmium, iron, copper, lead, zinc and nickel removal were 90, 80, 91.7, 91.6, 87.18, and 73.62% with 2.0 g/L MBK400, 1.0 g/L MBK400, 3.0 g/L MBK600, 2.0 g/L MBK600, 3.0 g/L MBK600 and 1.0 g/L MBK600, respectively. The removal of lead ranked the highest, consistently, for all the doses of MBK400 and MBK600 used. The Langmuir Type-1 was the most suitable linearized Langmuir isotherm that described the adsorption of the heavy metals in the DIWW, based on coefficient of determination (R^2). The adsorbents developed are suitable for the removal heavy metals, particularly lead, in a typical DIWW.

Keywords: Activated carbon; Adsorption; Dairy wastewater; Heavy metals; Milk bush kernel shell

1. Introduction

Dairy industries produce milk and ice cream products, using major raw materials such as sugar, milk fat, vegetable oil, sugar, cocoa powder, and chocolate paste. Concurrently, the industry produces large volumes of wastewater which is characterized by high organic load comprising of proteins, carbohydrates, amino acids, alkali metals, and phosphates as well as untreated milk, cheese, cream, and ice cream [1]. The presence of these pollutants gives the dairy industrial wastewater (DIWW) bad color and offensive odor, which have severe impacts on the receiving waters and the environment [2]. Some industrial wastewater containing heavy metals have proved challenging to some treatment

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*Corresponding author.

processes such as conventional biological process [3]; however, the application of adsorption process has attracted interest in recent times [4].

Commercial carbon used as adsorbents is relatively expensive and very difficult to regenerate, thus, spurred the search for cheaper alternatives. The suitability of any material for use as activated carbon is based on its high carbon contents and agricultural wastes such as cherry stones, rice husk, flamboyant pods, olive husks, milk bush kernel shell, and others which serve as good and efficient adsorbents when processed into activated carbon have been exploited for this purpose [5]. These materials serve as substitute to expensive activated because they are renewable, usually available in large amounts and less expensive.

Most commonly applied isotherms models include Langmuir, Freundlich, Temkin, Dubnin–Radushkevich, and Redlich–Peterson isotherm models used to study the nature of adsorption of various pollutants in the wastewaters [5–12]. These model equations which are always in nonlinear forms are usually linearized for effective evaluation of the model terms in the equations [13]. The linearization of the nonlinear models leads to rationalization of certain variables in the model, and this influence the understanding of the adsorption process [13].

The main aim of this study was to treat DIWW, which contains heavy elements such as cadmium, lead, nickel, zinc, iron, and copper, using activated carbon produced from milk bush kernel shell. The activated carbon was produced purposely for the removal of heavy metals present in the DIWW. Previous studies on the treatment of DIWW effluents through adsorption paid little attention to the removal of the heavy metals in the DIWW treated [14]. The adsorption characteristic of these pollutants was investigated with the four types of the linearized forms of Langmuir Isotherm.

2. Materials and methods

2.1. Materials

The raw DIWW was obtained from the production plant end pipe connected to equalization pond, at UAC Dairies, Oregun, Lagos, Nigeria. The dairy plant is one of the leading dairy manufacturers and produces a wide variety of dairy products but predominantly yoghurt products in different flavors. The DIWW was collected in a black container and brought to the Chemical Engineering Laboratory, Ladoke Akintola University of Technology, LAUTECH, Ogbomoso, Nigeria, where it was kept at a temperature of 4˚C until use. The initial concentrations of the selected heavy metals in the DIWW were characterized. The Milk bush kernels, collected from under its trees, in Ogbomoso, Oyo State, Nigeria, were processed by breaking the hard mesocarp to obtain the shells needed for the research work.

2.2. Methods

2.2.1. Preparation of activated carbon

The milk bush kernel shells (MBK) were washed thoroughly with tap water and later with distilled water to remove debris, left-over rinds, and other impurities from the shell. They were sun-dried for 3 d and later oven-dried overnight before crushing into smaller chips [5,12,15]. Dried shells samples (1.5 kg) were carbonized in the furnace (ISOTEMP Muffle Furnace Model 184A, UK) for 2 h at 400 and 600˚C, respectively. The carbonized samples were weighed afterward to determine the percentage burnt-off [5] before being crushed to uniform sizes. The carbonized sample (150 g) was mixed with H_3PO_4 (1 M) in the ratio 1:12 and then transferred into an oven set at temperature of 160˚C for a 24 h to form slurry which was washed with distilled water thoroughly until the solution pH was stable. The pH and conductivity of the acid-activated carbon were determined using pH meter (HACH senSion5) and conductivity meter (HACH senSion5), respectively. The acid-activated carbon (MBK) obtained was dried for 15 h. in the oven at about 110˚C, cooled at room temperature and stored for use.

2.2.2. Batch adsorption

Sample of the DIWW collected was stirred vigorously, allowed to settle for about 24 h and transferred to 25 l basin, which served as a preliminary settling tank, and then. The MBK-activated carbon (0.1 g) produced at 400˚C (MBK400) was added to 100 ml of the DIWW in 250-ml conical flask and then agitated with a magnetic stirrer at 120 rpm for 5-, 10-, 15-, 20-, and 25-min intervals. The procedure was repeated for 0.2 and 0.3 g of MBK400 and subsequently, for the activated carbon produced at 600˚C (MBK600). The samples were filtered, after each adsorption period, using Whatman No1 filter paper, and the filtrates were analyzed for the amount of the selected heavy metals removed using the Atomic Absorption Spectrometer (Alpha Model) at the Central Research Laboratory, LAUTECH, Ogbomoso, Nigeria. The effect of adsorbent dose and time on the pH and conductivity of the DIWW sample was determined, while the percentage removals of the selected heavy metals were quantified according to Eq. (1).

Table 1
Initial concentrations of heavy metals in raw DIWW

Sample	Cd (mg/L)	Fe (mg/L)	Cu (mg/L)	Pb (mg/L)	Zn (mg/L)	Ni (mg/L)
Raw wastewater	0.090	1.181	0.350	1.095	0.234	0.166

Table 2
pH and conductivity of activated carbon

Samples	pH	Conductivity (mS/cm)
MBK400	8.1	0.437
MBK600	8.5	0.224

$$\text{Removal efficiency} = \frac{C_r - C_t}{C_r} \times 100 \quad (1)$$

where C_r and C_t are concentrations of trace metal in raw and treated wastewater, respectively.

3. Result and discussion

The selected physico-chemical characteristics of the DIWW collected are presented in Table 1. The results indicate that the DIWW is weakly acidic (pH 6.07) and the initial concentrations of the selected heavy metals in the DIWW are above acceptable standards.

3.1. Effect of activation process on pH and conductivity of activated carbon

The pH and conductivity of the activated carbon produced from Milk bush kernel shell (MBK400 and MBK600) are illustrated in Table 2. The pH of the MBK-activated carbon increased (8.1–8.5) as the carbonization temperature increased (400–600˚C), while the conductivity decreased (72.86–79.78 mS/cm), respectively.

3.2. Effect of adsorption processes on pH and conductivity of DIWW

Generally, the pH of the treated DIWW increased at the end of the adsorption period beyond the initial pH of 6.1 to the ranges of 6.7–6.9 and 6.8–6.9 with MBK400 and MBK600, respectively (Fig. 1). These indicate slight changes in the acidic nature of the raw DIWW; however, these ranges are slightly less than the range (pH 7.0–8.5) set by World Health Organization (WHO). The treated DIWW may be acceptable for discharge into aquatic environment since the pH ranges obtained are within the European Union (EU) limits (pH 6.0–9.0), sets for fisheries and aquatic life [16]. The effect of increasing dose of MBK400 on the final pH of the treated DIWW did not follow any fixed pattern, while MBK600 showed decreased pH (6.9–6.8) as the dose increased from 1.0 to 3.0 g/L. This development suggests that the initial pH of the activated carbon might not be a contributing factor to the changes in the pH of the treated DIWW, and as a result, the addition of adsorbents has little or no effect on the pH of treated DIWW.

The changes in the conductivity of the treated DIWW with various doses (1.0–3.0 g/L) of MBK400 and MBK600, respectively, were not too orderly,

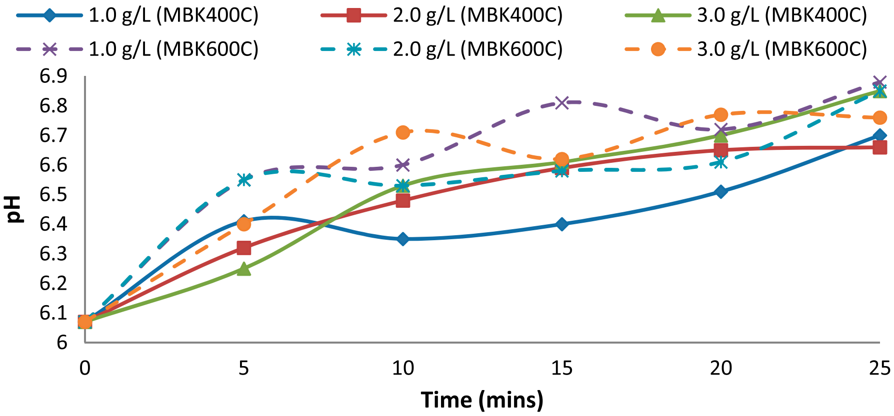

Fig. 1. Effect of adsorbent dose on pH of treated DIWW.

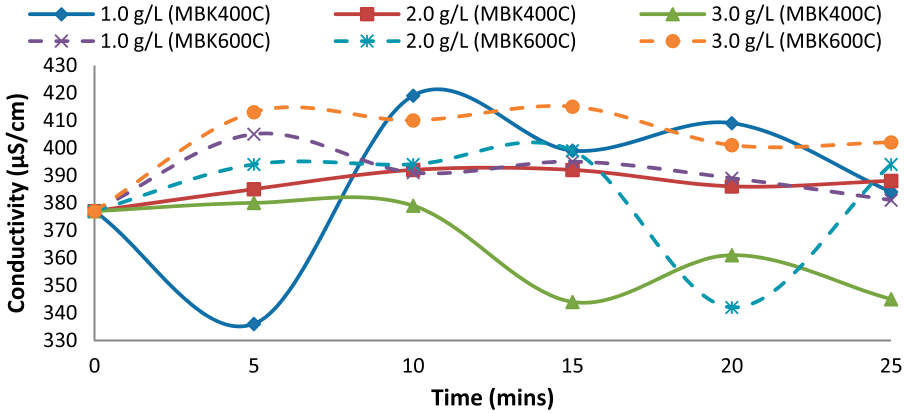

Fig. 2. Effect of adsorbent dose on conductivity of treated DIWW.

particularly with respect to time; however, at the end of the adsorption period, there were slight increase in the conductivity of the treated DIWW, except with 3.0 g/L of MBK400, which finally reduced the conductivity of the raw DIWW beyond the initial value of 377–345 µS/cm (Fig. 2). The effect of dose of MBK400 on the final conductivity of the treated DIWW did not follow order of increasing dose (1.0–3.0 g/L), while the increasing dose of MBK600 increased the conductivity (381–402 µS/cm) of the treated DIWW. Similar trend was reported by Qasim and Mane [14] who treated dairy wastewater with 0.5–3.0 g/L of powdered-activated charcoal and conductivity of 676.5 µS/cm was obtained with 0.5 g/L. The conductivity increased to 729.5 µS/cm with 1.5 g/L of the powdered-activated charcoal, but decreased to 694.5 µS/cm with 3.05 g/L. Treated effluent with lower conductivity (≤250 µS/cm) is generally favoured for discharge into receiving water bodies [16].

3.3. Effect of adsorbent dose on percentage removal of heavy metal in DIWW

The percentage (%) removal of cadmium from DIWW increased with agitation time (5–20 min) for all the doses of adsorbents (Fig. 3). The highest percentage removal (90%) was obtained for cadmium with 2.0 g/L of MBK400 and 1.0 g/L of MBK600, respectively. The application of 2.0 g/L of MBK400 may be preferred, if the ultimate choice is to remove cadmium from DIWW, though lesser dose of MBK600 was required; however, the cost of raising a temperature of the material to from 400 to 600˚C might not be cost-effective, industrial-wise. Furthermore, there was a rapid removal of cadmium within the first 10 min with 2.0 g/L dose of MBK400 better than 1.0 g/L dose of MBK600 within same period.

The effect of dose (1.0–3.0 g/L) of adsorbents (MBK400 and MBK600), at various agitation time, on removal of iron in the DIWW showed rapid removal

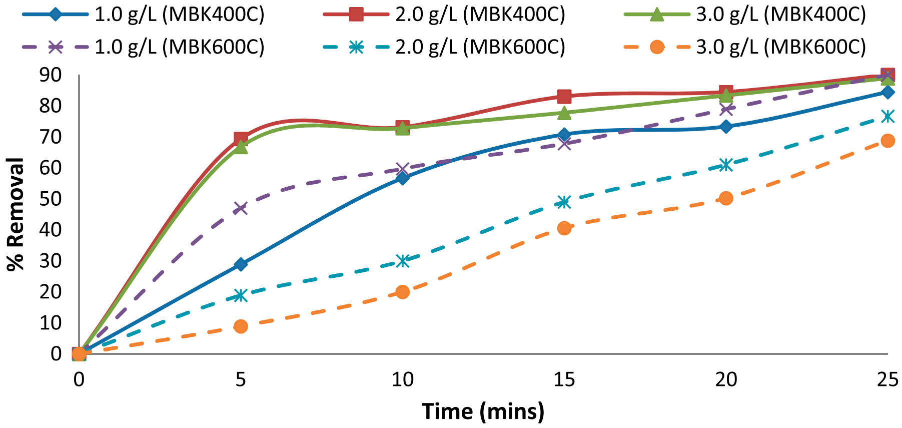

Fig. 3. Effects of adsorbent (MBK) dose on percentage removal of cadmium.

within the first 5 min and then a gradual increased as the agitation time increased (Fig. 4). The 2.0 g/L of MBK600 showed no removal in the first 5 min with the 2.0 g/L of MBK600, but this improved thereafter to 79.8% which is very close to the highest percentage removal (80%) obtained with 1.0 g/L of MBK400. The maximum percentage removal obtained with 3.0 g/L MBK400, 1.0 g/L MBK600, 2.0 g/L MBK600, and 3.0 g/L MBK600 were 73.66, 54.12, 51.78, and 64.26%, respectively. The percentage removals obtained for MBK400 were generally higher than those obtained for MBK600. There was decrease in the removal efficiencies of the MBK400 with increased dose and time, while the removal efficiencies of the MBK600 did not follow any trend for the removal of iron from DIWW. It may be inferred that MBK400 is suitable for the removal of iron in DIWW, if it the sole targeted pollutant.

The percentage removal of copper from DIWW generally increased rapidly within the first 5 min for all the doses of MBK400 and MBK600 except 3.0 g/L of MBK600 which increased after the first 5 min to 91.7% removal in the system (Fig. 5). The maximum percentage removal of copper were 61.71, 51.63, and 71.14% with 1.0, 2.0, and 3.0 g/L MBK400, respectively, and these were correspondingly lower than the percentage removal (76.57, 66, and 91.71%) obtained from the application of for 1.0, 2.0, and 3.0 g/L MBK600, respectively. Generally, percentage removal decreased from 1.0 to 2.0 g/L then increased from 2.0 to 3.0 g/L, for both MBK400 and MBK600 as the agitation time increased. This further suggests that the carbonization temperature of the selected adsorbents may be a contributing factor for the removal of copper from DIWW.

The percentage of lead removed from the treated DIWW increased almost serially with increased agitation time for all the doses of the adsorbents (MBK400 and MBK600), except for 1.0 and 3.0 g/L of MBK600 which experienced rapid percentage removal within

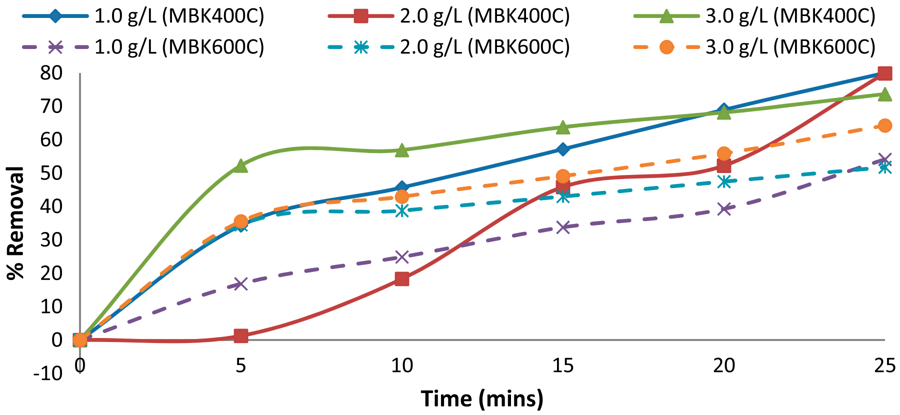

Fig. 4. Effects of adsorbent (MBK) dose on percentage removal of iron.

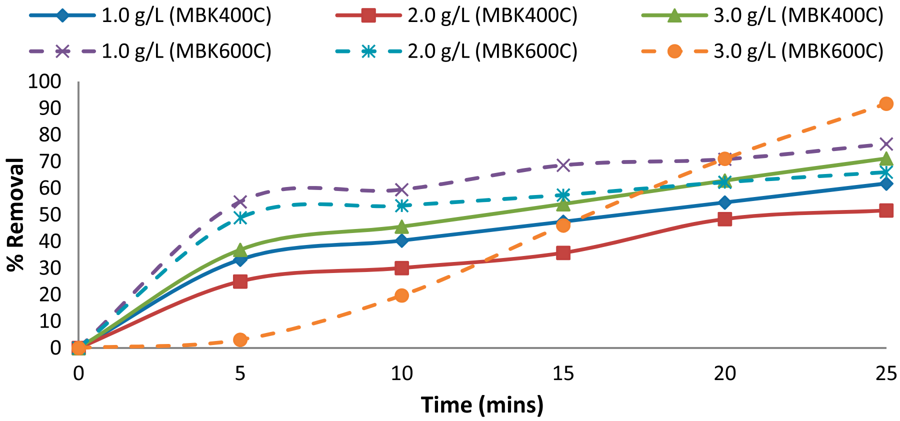

Fig. 5. Effects of adsorbent (MBK) dose on percentage removal of copper.

the first 7 min, before experiencing, almost constant change till the end of the study (Fig. 6). The maximum percentage removal of lead with 1.0 and 2.0 g/L of MBK400 were 37.23 and 29.77%, which are lower than the percentage (88.77 and 91.63%) removed with 1.0 and 2.0 g/L MBK600, respectively; however, the percentage lead (89.59%) removed with 3.0 g/L of MBK400 was higher than the percentage (70.37%), removed with 3.0 g/L of MBK600. The result obtained for 2.0 g/L MBK600 showed a rapid removal within the shortest period of agitation time, besides giving the highest percentage (91.63%) of lead removal, thus making it the preferred dose and adsorbent type for the selective removal of lead from DIWW.

A similar trend was exhibited by all the doses of MBK400 and MBK600 for the removal of zinc in DIWW, particularly in the first 7 min. This indicates that the adsorbent developed from MBK400 and MBK600 is generally suitable for the removal of zinc from DIWW (Fig. 7). The maximum percentages (85.47 and 87.18%) of zinc removed from the DIWW with 2.0 and 3.0 g/L of MBK600 were higher than the percentages (79.06 and 86.32%) removed with 2.0 and 3.0 g/L of MBK400, while the maximum percentage (75.68%) removed with 1.0 g/L of MBK400 was higher than the percentages (69.35%) removed with 1.0 g/L of MBK600. The maximum percentage of zinc removed from DIWW increased with increasing dose of adsorbent and the agitation time; furthermore, this may be upheld for the activation temperature.

The percentages (86.14, 81.33, and 47.05%) of nickel removed (Fig. 8) from DIWW decreased as the doses of MBK400 increased (1.0 and 3.0 g/L), while the percentages (73.62, 61.08, and 71.69%) of nickel removed with MBK600 did not indicate any corresponding trend; however, they were relatively lower, except for

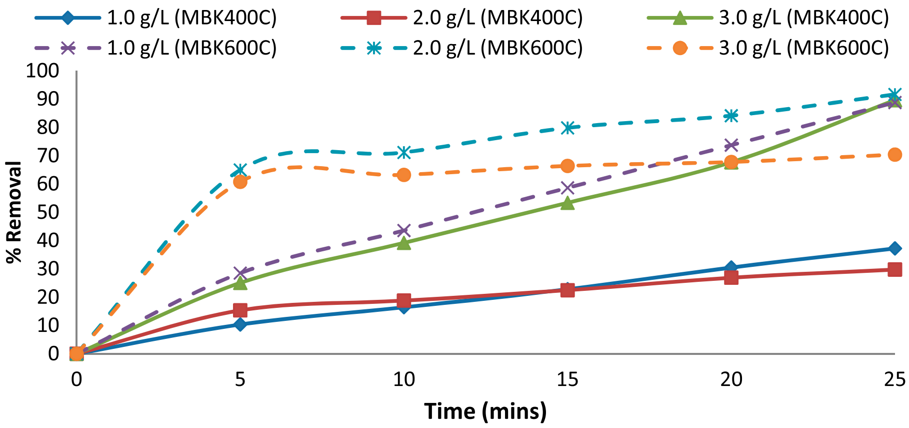

Fig. 6. Effects of adsorbent (MBK) dose on percentage removal of lead.

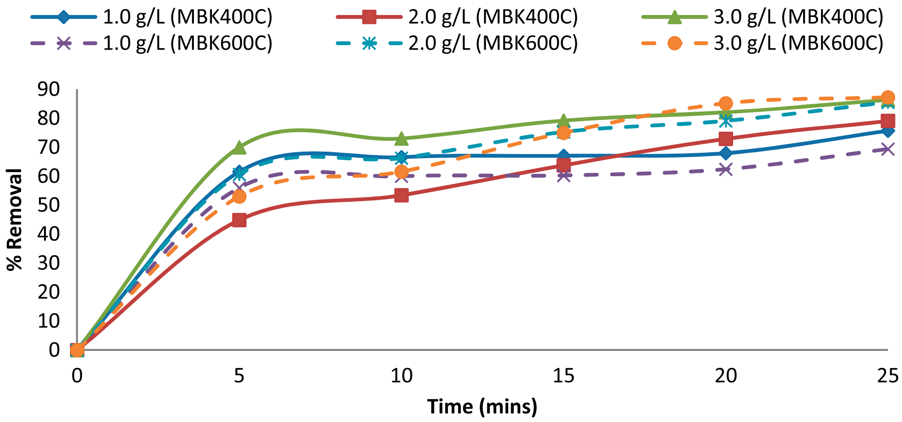

Fig. 7. Effects of adsorbent (MBK) dose on percentage removal of zinc.

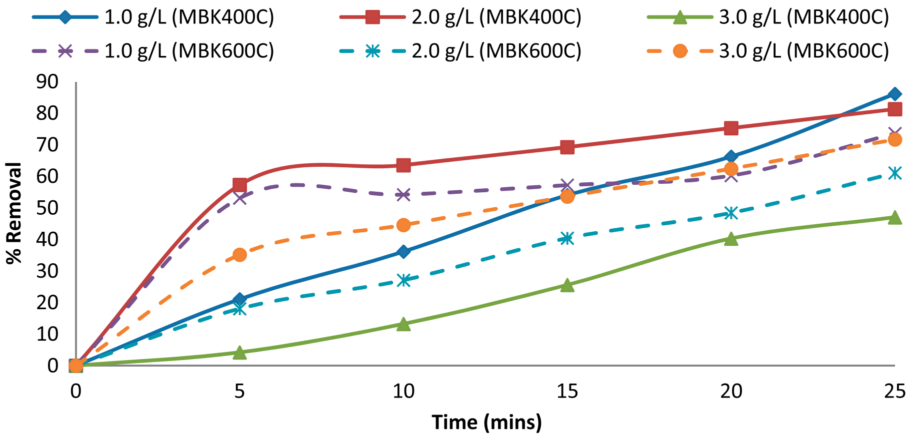

Fig. 8. Effects of adsorbent (MBK) dose on percentage removal of nickel.

percentage removal with 3.0 g/L of MBK600 which is higher than the percentage removed with 3.0 g/L of MBK400. Nickel removed from DIWW with 1.0 and 3.0 g/L of MBK400 as well as 1.0 g/L of MBK600 exhibit, almost, linear relationship with respect to the agitation time while 2.0 g/L of MBK400 as well as 2.0 and 3.0 g/L of MBK600 revealed rapid removal in the first 7 min. Thus, 2.0 g/L of MBK400 may be considered as the most suitable for the removal of nickel removed from DIWW, with respect to the dose, carbonization temperature, and percentage removal.

3.4. *Effect of contact time on the adsorption capacities-activated carbons (MBK400 and MBK600)*

The adsorption capacity of 1.0 g/L of MBK400 generally increased as the contact time increased and indicated highest (0.95 mg/g) and lowest (0.076 mg/g) capacity for the removal iron and cadmium, respectively, from DIWW. Iron adsorption was slightly rapid, initially, and increased as the contact time increased; however, only zinc experienced rapid adsorption at the first period of the process and then became stagnant till the end of the process (Fig. 9). The adsorption capacity of 2.0 g/L of MBK400 increased for all the selected heavy metals except for cadmium (Fig. 10). Similarly, all the metals, except iron and cadmium, experienced rapid adsorption at the first period of the process and increased till the end of the process, while nickel remained slightly steady and maximum adsorption capacity (1.63 mg/g) was obtained for lead. The trend of adsorption for 3.0 g/L of MBK400 was slightly similar to those exhibited by 2.0 g/L of MBK400, (Fig. 11). The maximum adsorption capacity (3.27 mg/g) was obtained for lead, and this indicates that adsorption capacity of 3.0 g/L of MBK400 was higher than 2.0 g/L of MBK400.

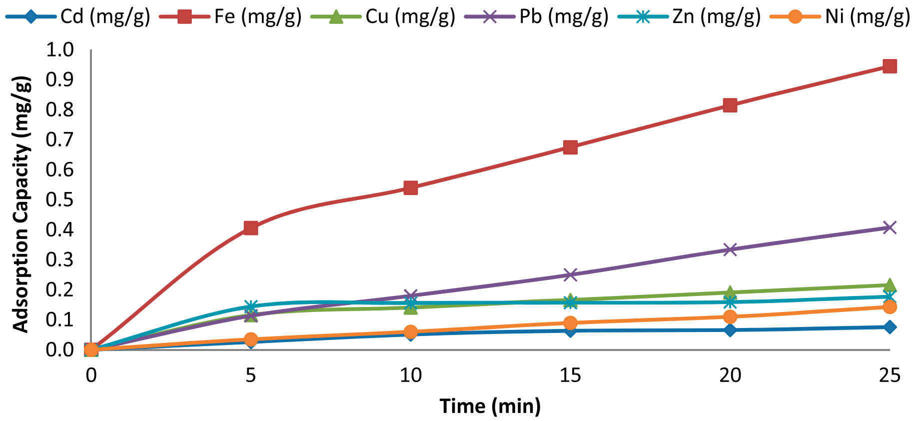

Fig. 9. Adsorption capacity of 1.0 g/L MBK400 (mg/g).

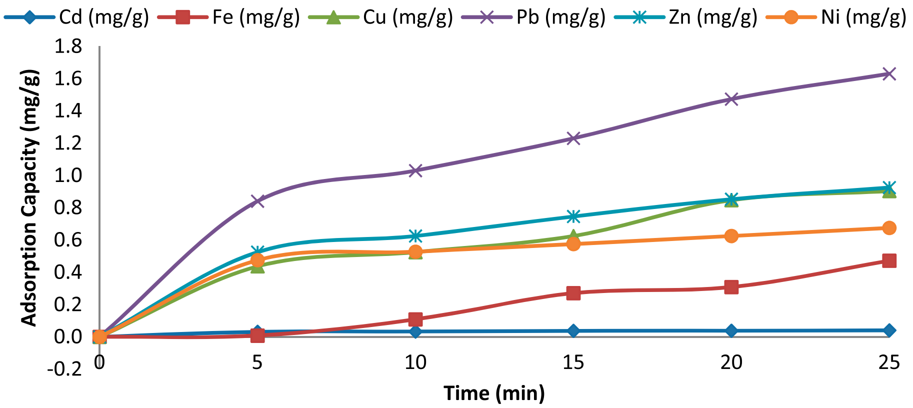

Fig. 10. Adsorption Capacity of 2.0 g/L MBK400 (mg/g).

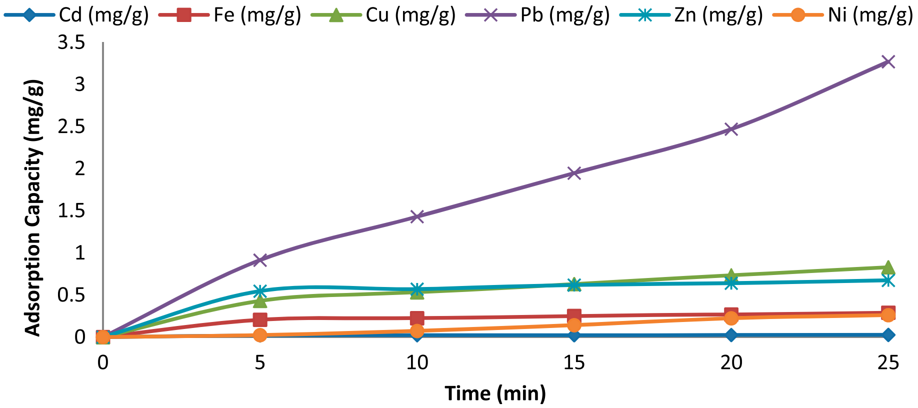

Fig. 11. Adsorption capacity of 3.0 g/L MBK400 (mg/g).

The adsorption capacity of 1.0 g/L of MBK600 increased as the contact time increased and showed slightly rapid adsorption at the first period of the process (Fig. 12). The adsorption of the metals, except lead and iron, later became constant till the end of the process. The maximum adsorption capacity (0.97 mg/g) was obtained for lead. This is very close to the maximum adsorption capacity (0.95 mg/g)

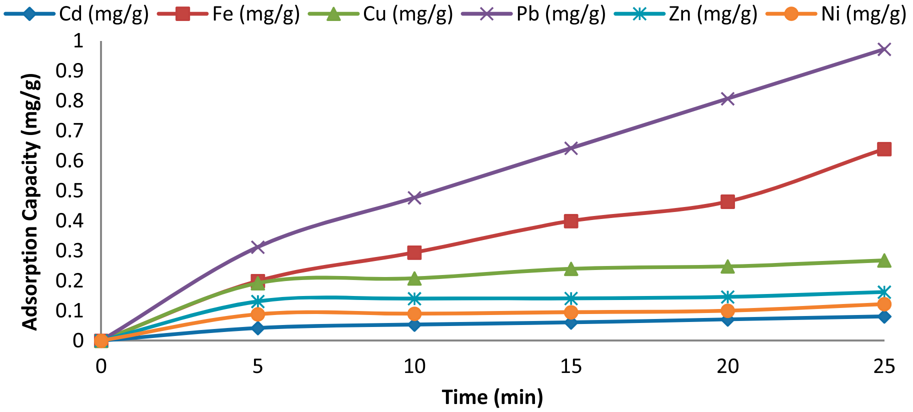

Fig. 12. Adsorption capacity of 1.0 g/L MBK600 (mg/g).

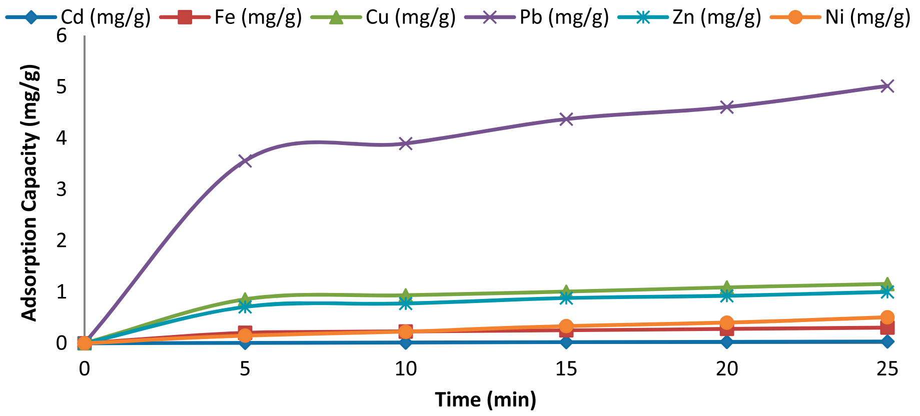

Fig. 13. Adsorption capacity of 2.0 g/L MBK600 (mg/g).

obtained for iron with 1.0 g/L of MBK400, and this suggest that the doses of the adsorbents influence the adsorption capacities of adsorbents. The adsorption capacity of 2.0 g/L of MBK600 was found to be too rapid for lead at the first period of the process and increased till the end of the process while copper and nickel exhibited less rapid adsorption (Fig. 13). On the other hand, the adsorption capacity for nickel and iron was linear while cadmium remained virtually unchanged. The maximum adsorption capacity of 5.02 mg/g was obtained for lead. The adsorption capacity revealed by 3.0 g/L of MBK600 (Fig. 14) was comparable to those exhibited by 2.0 g/L of MBK600 (Fig. 12), although the maximum adsorption capacity 2.57 mg/g obtained was slightly more than half the maximum capacity demonstrated by 2.0 g/L of MBK600 and the capacity became slightly stagnant with increase in contact time (Fig. 14).

The selection of adsorbents for the treatment of pollutants in wastewater is predominantly influenced by the removal efficiency, adsorption capacities and cost, among others [17]. Bhatt and Shah [4] noted that the typical rapid exchange rate in the beginning of the study can be well explained on the concept of law of mass action. The rate of adsorption is directly proportional to the surface area of the adsorbent, thus the initial faster rate of most of the metals, generally occurred as a result of the

Table 3
Langmuir isotherm types and their linear forms

Langmuir isotherm type	Linear form	Plot
Langmuir 1	$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K q_m}$	$\frac{C_e}{q_e}$ vs C_e
Langmuir 2	$\frac{1}{q_e} = \left[\frac{1}{K q_m}\right] \frac{1}{C_e} + \frac{1}{q_m}$	$\frac{1}{q_e}$ vs $\frac{1}{C_e}$
Langmuir 3	$q_e = q_m + \left[\frac{1}{K}\right] \frac{q_e}{C_e}$	q_e vs $\frac{q_e}{C_e}$
Langmuir 4	$\frac{q_e}{C_e} = K q_m + K q_e$	$\frac{q_e}{C_e}$ vs q_e

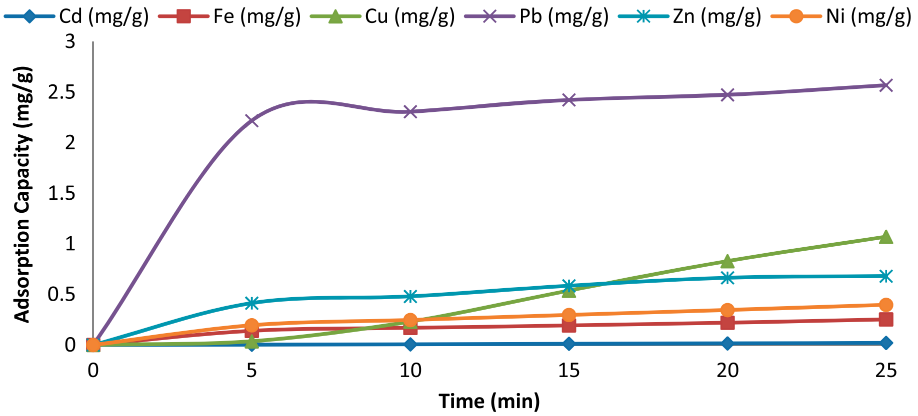

Fig. 14. Adsorption capacity of 3.0 g/L MBK600 (mg/g).

Table 4
Langmuir isotherm parameters obtained from the linearized forms for MBK400

Heavy metals	Adsorbent dose (g/L)	Langmuir 1			Langmuir 2			Langmuir 3			Langmuir 4			Remarks (most fit)
		q_m (mg/g)	K (L/mg)	R^2	q_m (mg/g)	K (L/mg)	R^2	q_m (mg/g)	K (L/mg)	R^2	q_m (mg/g)	K (L/mg)	R^2	
Cd	1.0	0.021	−64.2	**0.936**	0.029	−93.9	**0.562**	0.035	−111.1	**0.781**	0.028	−87.2	**0.781**	Langmuir 1
	2.0	0.028	−294.1	**0.996**	0.029	−360.9	**0.854**	0.029	−370.4	**0.895**	0.028	−211.3	**0.729**	Langmuir 1
	3.0	0.018	−250.7	**0.993**	0.019	−313.6	**0.847**	0.019	−322.9	**0.902**	0.018	−353.6	**0.918**	Langmuir 1
Fe	1.0	0.333	−4.9	**0.941**	0.391	−6.4	**0.712**	0.418	−6.9	**0.890**	0.386	−6.2	**0.890**	Langmuir 1
	2.0[a]	0.007	−2.1	**0.532**	0.015	−3.4	**0.208**	0.109	−4.9	**0.799**	0.077	−3.9	**0.799**	Langmuir 3 and 4
	3.0[a]	0.152	−6.3	**0.991**	0.157	−6.7	**0.929**	0.159	−6.8	**0.970**	0.156	−6.6	**0.970**	Langmuir 1
Cu	1.0	0.073	−10.4	**0.967**	0.077	−11.0	**0.887**	0.080	−11.3	**0.973**	0.077	−11.0	**0.973**	Langmuir 3 and 4
	2.0	0.237	−7.7	**0.965**	0.245	−7.9	**0.922**	0.253	−8.0	**0.991**	0.249	−7.9	**0.991**	Langmuir 3 and 4
	3.0	0.311	−13.9	**0.963**	0.339	−15.5	**0.838**	0.353	−16.2	**0.949**	0.338	−15.4	**0.949**	Langmuir 1
Pb	1.0[a]	0.045	−1.5	**0.873**	0.048	−1.6	**0.803**	0.056	−1.6	**0.990**	0.054	−1.6	**0.990**	Langmuir 3 and 4
	2.0[a]	0.322	−1.5	**0.947**	0.231	−1.5	**0.982**	0.270	−1.5	**0.997**	0.268	−1.5	**0.997**	Langmuir 3 and 4
	3.0[a]	0.868	−5.6	**0.861**	1.222	−12.4	**0.445**	1.409	−14.3	**0.770**	1.231	−11.0	**0.770**	Langmuir 1
Zn	1.0	0.110	−44.9	**0.994**	0.113	−47.3	**0.949**	0.113	−47.9	**0.977**	0.026	−14.2	**0.380**	Langmuir 1
	2.0	0.421	−31.8	**0.976**	0.456	−36.8	**0.840**	0.469	−38.3	**0.932**	0.449	−35.7	**0.932**	Langmuir 1
	3.0	0.470	−93.4	**0.997**	0.482	−103.7	**0.921**	0.484	−105.3		0.477	−99.8	**0.948**	Langmuir 1
Ni	1.0	0.032	−29.7	**0.849**	0.046	−54.9	**0.448**	0.056	−64.9	**0.784**	0.048	−50.9	**0.784**	Langmuir 1
	2.0	0.389	−67.6	**0.989**	0.408	−76.5	**0.886**	0.413	−78.1	**0.942**	0.403	−73.8	**0.942**	Langmuir 1
	3.0	0.013	−10.5	**0.684**	0.016	−11.1	**0.561**	0.028	−12.1	**0.978**	0.025	−11.8	**0.978**	Langmuir 3 and 4

[a] Not at the equilibrium.

Table 5
Langmuir isotherm parameters obtained from the linearized forms for MBK600

		Langmuir 1			Langmuir 2			Langmuir 3			Langmuir 4			
Heavy metals	Adsorbent dose (g/L)	q_m (mg/g)	K (L/mg)	R^2	q_m (mg/g)	K (L/mg)	R^2	q_m (mg/g)	K (L/mg)	R^2	q_m (mg/g)	K (L/mg)	R^2	Remarks (most fit)
Cd	1.0	0.039	−131.1	**0.960**	0.046	−226.4	**0.637**	0.048	−243.9	**0.800**	0.044	−195.9	**0.800**	Langmuir 1
	2.0	0.007	−41.8	**0.869**	0.009	−55.1	**0.590**		−62.9	**0.876**	0.012	−32.4	**0.925**	Langmuir 4
	3.0	0.002	−28.5	**0.754**	0.003	−35.0	**0.496**	0.006	−23.7	**0.919**	0.004	−37.1	**0.900**	Langmuir 3
Fe	1.0[a]	0.113	−1.9	**0.875**	0.129	−2.2	**0.736**	0.149	−2.3	**0.966**	0.140	−2.2	**0.966**	Langmuir 3 and 4
	2.0	0.106	−2.6	**0.986**	0.109	−2.7	**0.957**	0.110	−2.7	**0.992**	0.109	−2.7	**0.992**	Langmuir 3 and 4
	3.0	0.091	−3.4	**0.967**	0.097	−3.7	**0.877**	0.101	−3.8	**0.968**	0.097	−3.6	**0.968**	Langmuir 3 and 4
Cu	1.0	0.146	−24.8	**0.992**	0.151	−26.5	**0.926**	0.153	−27.0	**0.964**	0.150	−26.1	**0.964**	Langmuir 1
	2.0	0.568	−15.9	**0.992**	0.580	−16.4	**0.959**	0.584	−16.6	**0.986**	0.578	−16.4	**0.986**	Langmuir 1
	3.0	0.042	−10.7	**0.551**	0.089	−31.3	**0.171**	0.321	−44.4	**0.679**	0.217	−30.2	**0.679**	Langmuir 3 and 4
Pb	1.0[a]	0.289	−6.1	**0.897**	0.391	−11.7	**0.501**	0.444	−13.4	**0.770**	0.384	−10.3	**0.770**	Langmuir 1
	2.0	3.254	−22.3	**0.990**	3.539	−33.3	**0.756**	3.579	−34.5	**0.832**	3.435	−28.7	**0.832**	Langmuir 1
	3.0	1.558	−7.7	**0.998**	1.569	−7.8	**0.984**	1.572	−7.9	**0.993**	1.566	−7.8	**0.993**	Langmuir 1
Zn	1.0	0.092	−31.5	**0.995**	0.094	−32.5	**0.966**	0.094	−32.7	**0.987**	0.093	−32.3	**0.987**	Langmuir 1
	2.0	0.605	−62.9	**0.991**	0.641	−75.0	**0.857**	0.648	−77.5	**0.914**	0.629	−70.6	**0.914**	Langmuir 1
	3.0	0.368	−59.7	**0.985**	0.396	−73.0	**0.837**	0.404	−75.8	**0.913**	0.388	−69.1	**0.913**	Langmuir 1
Ni	1.0	0.066	−47.9	**0.993**	0.067	−49.9	**0.957**	0.068	−50.5	**0.985**	0.067	−49.6	**0.985**	Langmuir 1
	2.0	0.095	−16.2	**0.891**	0.111	−17.9	**0.730**	0.129	−19.3	**0.951**	0.118	−18.4	**0.951**	Langmuir 3 and 4
	3.0	0.142	−28.5	**0.956**	0.157	−32.4	**0.813**	0.165	−34.0	**0.941**	0.157	−32.0	**0.941**	Langmuir 1

[a] Not at the equilibrium.

available area on the surface of the adsorbents at the beginning [18]. Generally, all doses of MBK400 and MBK600 exhibited higher and lowest adsorption capacities for lead and cadmium, respectively, as the contact time increased. Related study on sorption of heavy metals (cadmium, lead, nickel, zinc, and copper) on resin indicated that 100% removal rate in the order $\mathrm{Cu} > \mathrm{Pb} \approx \mathrm{Zn} > \mathrm{Ni} \approx \mathrm{Cd}$ [4]. This further indicated that the adsorbents developed are more suitable for the removal lead, than cadmium, in a typical DIWW.

3.5. Adsorption isotherm study

Four types of Langmuir isotherm models were used to fit the adsorption of the heavy metals in the DIWW with MBK400 and MBK600 developed, in order to describe with precision, the suitability of the adsorption isotherm. The Langmuir equation is one of the commonly used isotherm modeling derived from simple mass kinetics. It assumes chemisorption and predicts a monolayer sorption capacity, at higher concentrations [19]. It is a two-parameter isotherm models, generally expressed as in Eq. (2).

$$q_e = \frac{q_m K C_e}{1 + K C_e} \tag{2}$$

where q_e is the amount of solute adsorbed per unit weight of adsorbent at equilibrium (mg/g), C_e is the equilibrium concentration of the solute in the bulk solution (mg/L), q_m is the maximum adsorption capacity (mg/g), and K is the constant related to the free energy of adsorption (L/mg).

The Langmuir isotherm equation was linearized into four forms ((Type-1, Type-2, Type-3, and Type-4) in order to estimate the two parameters (q_m and K) of the model [20,21]. Linear coefficient (R^2) usually shows the fit between experimental and calculated values of the linearized isotherm model. The Langmuir parameters (q_m and K) are obtained by plotting 'C_e/q_e vs. C_e' '$1/q_e$ vs. $1/C_e$' 'q_e vs. q_e/C_e' and 'q_e/C_e vs. q_e' for the linearized Langmuir Type-1, Type-2, Type-3, and Type-4, equations, respectively (Table 3).

The calculated parameters from the plots for the adsorption of the heavy metals (Cd, Fe, Cu, Pb, Zn, and Ni) from DIWW on various doses of MBK400 and MBK600 are shown in Tables 4 and 5, respectively. The suitability of the linearized Langmuir type was selected based on the coefficient of determination R^2 (Bold), and the adsorption of the heavy metals in DIWW fitted well in the order: Langmuir 1 > Langmuir 3 ≈ Langmuir 4, while none fitted to Langmuir 2, for the two adsorbents. This further justifies that application of various linear forms of Langmuir equation significantly affect the evaluation of the Langmuir parameters [22].

4. Conclusion

The toxic heavy metals commonly found in typical DIWW was successfully treated through adsorption process using activated carbon produced from milk bush kernel shell (MBK400 and MBK600) produced at 400 and 600°C. The study showed that the adsorption of the heavy metals was influenced by the dose, contact time, and activation temperature. The application of the adsorbent developed in this study indicates that the use of agricultural-based adsorbents is very effective in the treatment of the DIWW. The selected agricultural residue (milk bush kernel shell) is readily available, thus making the method affordable and less expensive. Therefore, the use of agricultural-based adsorbent, as viable alternatives to relatively expensive commercial carbon, in the treatment of DIWW, will be an economically competitive solution, because of their better removal efficiency in terms of their adsorption capacities.

References

[1] S.M. Khopkar, Environmental Pollution (Monitoring and Control), first ed., New Age International (P) Limited, Daryaganj, New Delhi, 2004.

[2] O.S. Amuda, I.A. Amoo, O.O. Ajayi, Performance optimization of coagulant/flocculant in the treatment of wastewater from a beverage industry, J. Hazard. Mater. B 129(1–3) (2006) 69–72.

[3] Y. Liu, Y.-J. Liu, Biosorption isotherms, kinetics and thermodynamics, Sep. Purif. Technol. 61 (2008) 229–242.

[4] R.R. Bhatt, B.A. Shah, Sorption studies of heavy metal ions by salicylic acid-formadehyde-catechol terpolymeric resin: Isotherm, kinetic and thermodynamics. Arabian J. Chem., 8(3) (2015) 414–426.

[5] A.O. Alade, O.S. Amuda, A.O. Ibrahim, Isothermal studies of adsorption of acenaphthene from aqueous solution onto activated carbon produced from rice (*Oryza sativa*) husk, Desalin. Water Treat. 46 (2012) 87–95.

[6] K.Y. Foo, B.H. Hameed, Insights into the modeling of adsorption isotherm systems, Chem. Eng. J. 156 (2010) 2–10.

[7] J.F. Porter, G. McKay, K.H. Choy, The prediction of sorption from a binary mixture of acidic dyes using single- and mixed-isotherm variants of the ideal adsorbed solute theory, Chem. Eng. Sci. 54(24) (1999) 5863–5885.

[8] V.C. Srivastava, M.M. Swamy, I.D. Mall, B. Prasad, I.M. Mishra, Adsorptive removal of phenol by bagasse

fly ash and activated carbon: Equilibrium, kinetics and thermodynamics, Colloids Surf., A: Physicochem. Eng. Aspects 272(1–2) (2006) 89–104.

[9] G. Bandyopadhyay, S. Chattopadhyay, Single hidden layer artificial neural network models versus multiple linear regression model in forecasting the time series of total ozone, Int. J. Environ. Sci. Technol. 4(1) (2007) 141–149.

[10] S. Gueu, B. Yao, K. Adouby, G. Ado, Kinetics and thermodynamics study of lead adsorption on to activated carbons from coconut and seed hull of the palm tree, Int. J. Environ. Sci. Technol. 4(1) (2007) 11–17.

[11] K. Vasanth-Kumar, S. Sivanesan, Isotherms for Malachite Green onto rubber wood (*Hevea brasiliensis*) sawdust: Comparison of linear and non-linear methods, Dyes Pigm. 72(1) (2007) 124–129.

[12] A.O. Alade, O.S. Amuda, T.J. Afolabi, A.A. Okoya, Adsorption of naphthalene onto activated carbons derived from milk bush kernel shell and flamboyant pod, J. Environ. Chem. Ecotoxicol. 4(7) (2012b) 124–132.

[13] B. Subramanyam, A. Das, Linearized and non-linearized isotherm models comparative study on adsorption of aqueous phenol solution in soil, Int. J. Environ. Sci. Technol. 6(4) (2009) 633–640.

[14] W. Qasim, A.A. Mane, Characterization and treatment of selected food industrial effluents by coagulation and adsorption techniques, Water Res. Ind. 4 (2013) 1–12.

[15] A.O. Alade, O.S. Amuda, O.O. Ogunleye, A.A. Okoya, Evaluation of interaction of carbonization temperatures and concentrations on the adsorption capacities and removal efficiencies of activated carbons using response surface methodology (RSM), J. Biorem. Biodegrad. 3 (2012) 134.

[16] A.O. Alade, A.T. Jameel, S.A. Muyibi, M.I. Abdul Karim, Z.M. Alam, Effect of biodegradation on the physical properties of palm oil mill effluent (pome) using mixed culture of fungi, J. Pure Appl. Microbiol. 8(Special Edition) (2014) 885–891.

[17] Metcalf and Eddy Inc. Wastewater Engineering: Treatment and Reuse, fourth ed., McGraw-Hill, New Delhi, (2003), 1138–1162.

[18] M.A.O. Badmus, T.O.K. Audu, B.U. Anyata, Removal of lead ion from Industrial wastewater by activated carbon prepared from periwinkle shells (*Typanotonus fuscatus*), Turkish J. Eng. Environ. Sci. 31 (2007) 251–263.

[19] P. Janos, H. Buchtova, M. Ryznarova, Sorption of dyes from aqueous solutions onto fly ash, Water Res. 37(20) (2003) 4938–4944.

[20] D. Ghosh, K.G. Bhattacharyya, Adsorption of methylene blue on kaolinite, Appl. Clay Sci. 20(6) (2002) 295–300.

[21] S.J. Allen, Q. Gan, R. Matthews, P.A. Johnson, Comparison of optimised isotherm models for basic dye adsorption by kudzu, Bioresour. Technol. 88 (2003) 143–152.

[22] Y.-S. Ho, Isotherms for the sorption of lead unto Peat: Comparison of linear and non-linear methods, Pol. J. Environ. Stud. 15(1) (2006) 81–86