Metals removal from automobile workshop stormwater runoff using rice husk, GAC and gravel filtration

Clement Oguche Ataguba and Isobel Brink

ABSTRACT

The efficiency of combined filtration media consisting of rice husk (RH), granular activated carbon (GAC) and gravel (GR) for the removal of metals cadmium, copper, lead and iron from stormwater runoff emanating from automobile workshops in Nigeria was investigated. Stormwater runoff samples were collected from five sites over a period of nine (9) weeks and filtered using two filter combinations, GAC – RH, GR – GAC as well as a RH-only filter. All the filters removed metals. Highest average singular metals removals were: approximately 74% copper for GR – GAC; 70% lead for RH, 67% iron for GAC – RH and 46% cadmium for GAC – RH. Average metals removal efficiencies (all metals combined) were GAC – RH 61%, GR – GAC 52% and RH-only 46%. The combined filter materials therefore showed better metals removal efficiencies than the RH-only filter. Further filtration of metals polluted stormwater would be required to lower the average metals concentration to meet local and international discharge standards. Future research into low cost modifications towards optimising the filter materials to improve metals removal efficiencies is recommended.

Key words | automobile workshop stormwater runoff, filtration, granular activated carbon, gravel, metals, rice husk

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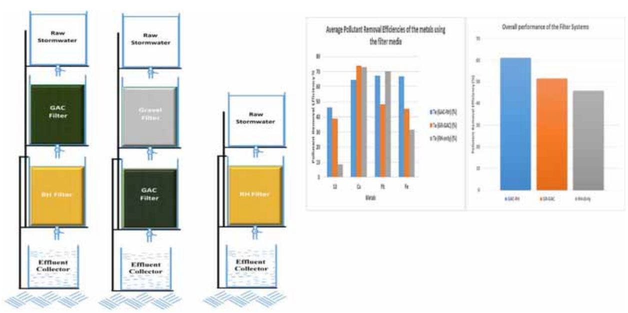
HIGHLIGHTS

- Untreated automobile stormwater runoff contribute immensely to surface water pollution.
- Development of low cost treatment technologies with locally available filter materials.
- Combined and single filter systems using locally available materials were designed and used.
- Combined filter system performed better than single filter system.
- Further research work is recommended in this area.

GRAPHICAL ABSTRACT



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INTRODUCTION

Two main categories of automobile maintenance centres exist in Nigeria, viz. mechanic villages and city-wide automobile workshops. City-wide automobile workshops are prominent in most urban centres in Nigeria. These workshops are typically located on unpaved natural soil surfaces under makeshift structures (trees, makeshift canopies or timber framed structures) close to a road. They are often poorly planned and lack services such as waste management and stormwater filtration facilities; thereby generating high environmental pollution (Iwegbue 2007; Udebuani *et al.* 2011).

The activities in these automobile workshops generate pollutants in gaseous, liquid and solid states, which can have adverse effects on the environment. Repairs, servicing and maintenance of automobiles are major sources of, *inter alia*, metals (metallic components of vehicle parts), used (waste) oil, chemical and inorganic additives and fuel (Brown & Peake 2006). These may be transported as pollutants in stormwater runoff and contribute to the deteriorating quality of the natural receiving water bodies, thereby adversely affecting their life support capabilities (Boroumant-Nasab 1995).

Metal compounds in stormwater can be a toxic and non-degradable addition to the environment (Muthukrishnan 2010). The removal of such potentially toxic metals from polluted stormwater is therefore necessary to protect both the environment and people who utilise local natural waterbodies. Different methods ranging from physical to electrochemical techniques have been researched to remove metals both in dissolved and suspended forms as well as other pollutants from stormwater (see Davis 2005; Wong *et al.* 2006; Abu-El-Halawa & Zabin 2017). Conventional methods such as reverse osmosis, ultrafiltration, electrodialysis, ion exchange, chemical precipitation, etc., as obtainable in developed countries, are uneconomical and technically cumbersome for use in developing countries (Brown *et al.* 2000; Fu & Wang 2011). Specifically, high capital/operating cost, regular energy requirements and lack of appropriate labour in the application of such technologies make such conventional techniques unsuitable for use in developing countries (Bahgat *et al.* 1999).

The use of low cost local options for filtration media has shown promise in reported case studies. In a study carried out by Min *et al.* (2007) to test the effectiveness of metals (Cd, Cu, Pb and Zn) removal in stormwater runoff using base-filtered juniper fibre (BTJF) media, it was found that the adsorption ability of the BTJF was substantial in the removal of all said metals. Ghrab *et al.* (2014) studied the adsorption of chromium and nickel ions from industrial wastewater on illitic Tunisian clay (MOM R). The results showed that the adsorbent performed very well and was recommended for use as an emerging water filtration technology. Hatt *et al.* (2007a) conducted experiments on a laboratory-scale gravel infiltration system to determine the pollutant removal efficiency under different water level regimes. The research showed that gravel filters were very effective in sediment and metals removal with respect to all water level regimes, with a singular disadvantage that the system clogged over time.

Research towards determining efficiencies of metals removal from stormwater using natural mineral based filter media has also been reported. In a study carried out by Haile & Fuerhacker (2018), the efficiencies of five selected filter media to adsorb metals from roadway stormwater runoff were evaluated using a column experiment. The filter media were natural quartz, sandy soil and three mineral-based technical filter media, while the metals considered were copper, lead and zinc. The results indicated that all the technical filters and the sandy soil performed very well in the removal of said metals while the natural quartz soil performed poorly.

Furthermore, the use of organic fibres from agricultural wastes have shown promise in reported studies. Agricultural byproducts, which have recorded success in their use as filter media as well as coagulant for surface/wastewater filtration, are sugarcane bagasse and banana pith (Hamid *et al.* 2016; Kakoi *et al.* 2016). These have been shown to be efficient in the removal of metals as well as oil and grease. In research carried out by Masoud *et al.* (2012), using both activated rice husk (RH) and activated carbon filter media in the removal of iron and manganese from wastewater, it was discovered that even though both filter media were efficient, the activated RH performed better.

Tran *et al.* (2017) carried out a study to ascertain the adsorption capacity and removal efficiency levels of copper, lead and nickel using sugarcane derived activated carbon. It was reported that the order of removal efficiency and adsorption capacity were in the order Pb (99.9%, 19.3 mg/g) > Cu (90%, 13.24 mg/g) > Ni^{2+} (66.4%, 2.99 mg/g). The study showed that activated carbon derived from the sugarcane bagasse is an efficient adsorbent for the removal of the metals considered.

Research by Rohaeti *et al.* (2016) showed that rice husk and rice husk ash adsorbed lead ions from a solution to maximum adsorption capacity levels of 28.7 mg/g and 51.5 mg/g, respectively. Similarly, Pathak *et al.* (2016) has reported that rice husk effectively removed an average of 92.5% of pollutants (other than metals) from diary wastewater. The maximum pollutants uptake from the diary wastewater was computed as 71.4 mg/g.

In terms of cost/adsorption capacity, granular activated carbon is more expensive and has higher adsorption capacity than rice husk. However, the use of rice husk as adsorbent in water treatment has been found to be less expensive/cost effective, naturally available in abundance and environmentally friendly than activated carbon (Ansari & Raofie 2006; Mathurasa & Damrongsiri 2018; Khalilzadeh *et al.* 2020). This adsorbent has rapid uptake and good adsorption capacity which makes it possible to be used as adsorption material whether in modified or unmodified form (Khan *et al.* 2004).

This research was carried out to evaluate the potentials of cadmium, lead, copper and iron removal from automobile stormwater runoff in Nigeria using low cost RH filter columns, granular activated carbon (GAC) – RH combined filter columns and gravel (GR) – GAC combined filter columns.

MATERIALS AND METHODS

RH-only filter column units, GAC – RH filter column units and GR – GAC filter column units were designed and built to treat stormwater runoff samples collected over a period of nine (9) weeks during the rainy season from five selected automobile workshops in Nigeria. Details of the filter designs as described in Ataguba & Brink (2020) are presented in Table 1.

Three automobile workshops were selected from Idah Town of Nigeria (labelled Automobile Workshops 1 to 3) and two others were selected from Lokoja Town of Nigeria (labelled Automobile Workshops 4 and 5). Both towns are on the bank of River Niger, one of the two major rivers in Nigeria. Stormwater catch-pits were created at the downstreams of the selected automobile workshops for easy collection of runoff samples.

Table 1 | Details of design equations, data and references for the filter designs

Filter	Design equation	Design data		Reference
GR filter design	$V_f\left(\frac{m}{h}\right) = \frac{Q}{A} = Q \div \frac{\pi D^2}{4}$ $\textbf{Density } \boldsymbol{\rho} = \frac{Mass\ (m)}{Volume\ (v)}$	Depth of column Height of filter Freeboard Diameter of column Volume of gravel Density of gravel Mass of gravel Filtration rate Flow rate	$H = 0.40$ m $L = 0.3$ m $t = 0.10$ m $D = 0.10$ m $V_G = 0.0024\ m^3$ $\rho_G = 1{,}400\ kg/m^3$ $M_G = 3.4$ kg $V_f = 1.0$ m/h $Q = 0.008\ m^3/h$	Wegelin (1996); Density-Mass-Volume relation
GAC filter design	$EBCT = \frac{V}{Q} = \frac{A \times L}{Q}$ $\textbf{Density } \boldsymbol{\rho} = \frac{Mass\ (m)}{Volume\ (v)}$	Depth of column Height of column Freeboard Diameter of column Volume of GAC Density of GAC Mass of GAC Empty bed contact time (EBCT)	$H = 0.40$ m $L = 0.30$ m $t = 0.10$ m $D = 0.10$ m $V_{GAC} = 0.0024\ m^3$ $\rho_{GAC} = 650\ kg/m^3$ $M_{GAC} = 3.4$ kg =18 mins	USACE (2001); Density-Mass-Volume relation
RH filter design	$\textbf{Density } \boldsymbol{\rho} = \frac{Mass\ (m)}{Volume\ (v)}$	Depth of column Height of filter Freeboard Diameter of column Volume of RH Density of RH Mass of RH Filtration rate Flow rate	$H = 0.40$ m $L = 0.30$ m $t = 0.10$ m $D = 0.10$ m $V_{RH} = 0.0024\ m^3$ $\rho_{RH} = 100\ kg/m^3$ $M_{RH} = 0.24$ kg $V_f = 1.0$ m/h $Q = 0.008\ m^3/h$	Density-Mass-Volume relation

Briefly, the setup included cylindrical columns made from PVC pipes; 0.3 m length and 0.1 m diameter (Figure 1), containing the different filtration media. All filter materials (RH, carbon and 12 mm river gravel) were low-cost and locally sourced as reported in Ataguba & Brink (2020). The raw carbon (from wood combustion), locally obtained from charcoal vendors, was converted to granular form and activated via thermal activation (pyrolysis) as described in McDougall (1991). RH, which is waste from rice processing, was obtained from the rice mill in Idah, Nigeria at no cost. River gravel was obtained from river gravel mining site at Idah, Nigeria. The river gravel and RH were washed with water and dried before use in the filter columns. The sizes of the filter materials used in this research were 2.40 mm (BS Sieve No. 8), 0.40 (BS Sieve No. 40) and 12 mm for the GAC, RH and GR, respectively. Commercially available 100 mm diameter polyvinyl chloride (PVC) pipes which were used for the construction of the filter columns were also sourced from the local market in Idah, Nigeria.

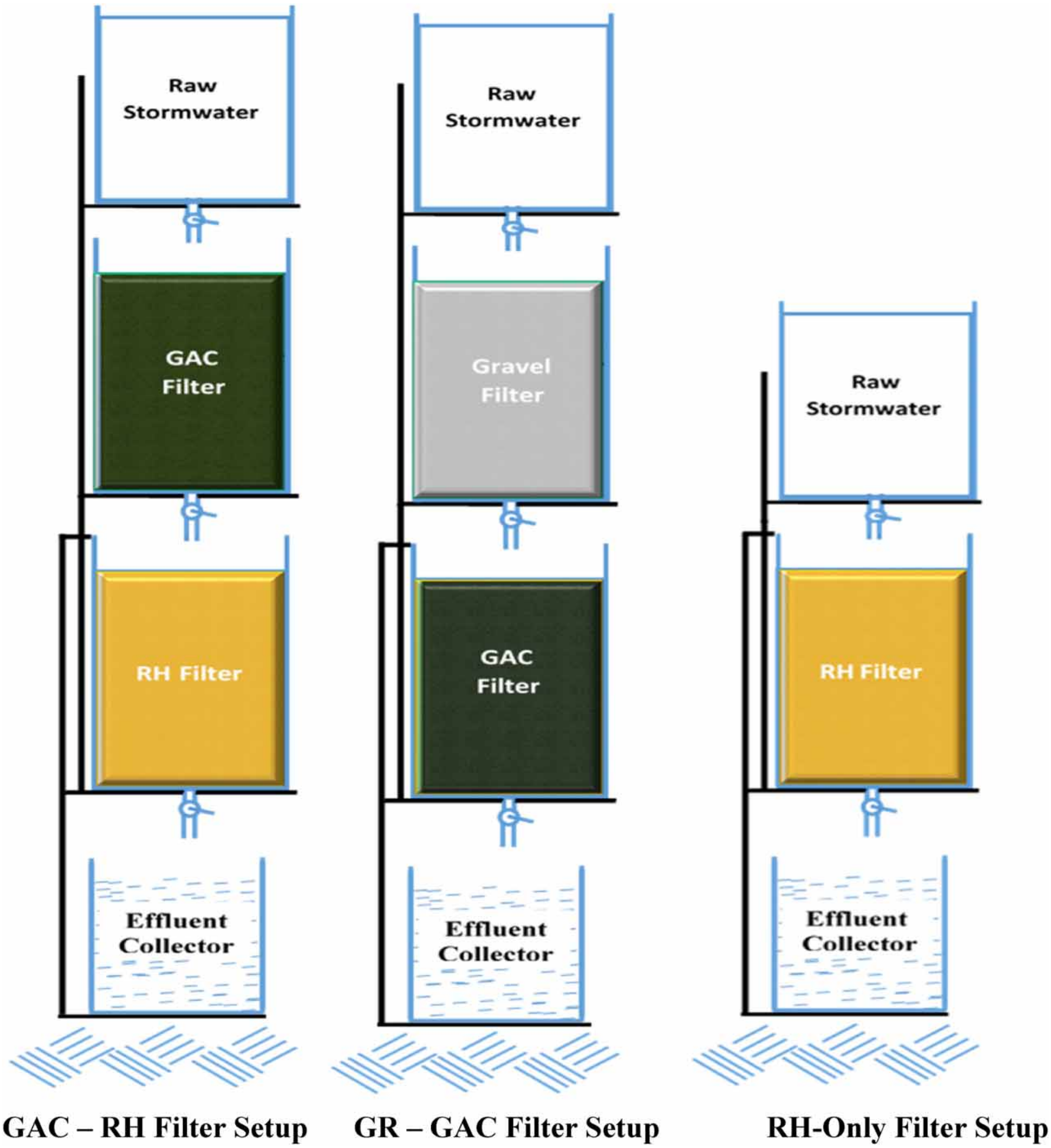

Figure 1 | Filtration systems. GAC – RH filter, Setup GR – GAC filter setup, RH-Only filter setup.

Three stormwater runoff samples were collected in 1.5 L laboratory bottles from each automobile workshop weekly for analyses. The raw samples collected were passed through the different filter column setups (Figure 1) and the treated effluents were collected and analysed. A total of 10 samples for stormwater quality experiments (two tests per heavy metal per filter system per automobile workshop) were collected and tests carried out on a weekly basis over the period of nine weeks. Similarly, a total of 10 samples for raw stormwater quality experiments for the selected automobile workshops (two tests per automobile workshop) were obtained and tests carried out on weekly basis over the period of nine weeks to determine the untreated stormwater quality. The tests were carried out in duplicates and the average concentration of the heavy metals before and after filtration over the entire nine weeks were computed and used for the analyses. The water treatment processes of granular filtration and adsorption as described in Crittenden *et al.* (2012) were adopted for this research. The treatment of the stormwater runoff sample by the river gravel was granular filtration while the treatment process by the rice husk and GAC was adsorption. The overall results desired was to determine the concentration of the metals under study before and after these treatments. The columns were operated under gravity flow conditions. The filter set-ups were allowed to run for 45 min before the effluent collecting jars were removed and taken for analysis. The flow rate was set at $0.008\,m^3/h$ (Ataguba & Brink 2020). This process was repeated for all samples from the automobile workshops throughout the entire research period. The filter materials were replaced after every single treatment instead of being regenerated as it is economical and materials are available at little or no cost. The pre-filtration (raw) and post-filtration (treated) samples were analysed for cadmium, copper, lead and iron in accordance with APHA (2017) using an ICE 3000 Series AA Spectrometer (Flame Atomic Absorption Spectrometry technique) This spectrometer has the following detection limits for the metals tested: cadmium (0.001 mg/L); lead (0.05 mg/L); copper (0.01 mg/L) and iron (0.02 mg/L). Analyses were conducted in the Water Quality Control Laboratory at the National Geosciences Research Laboratories in Kaduna, Nigeria.

The average results from the pre-filtration and post-filtration samples over the entire period of nine weeks (average of nine storm events) were analysed and are presented. Additionally, pollutant removal efficiencies for the metals were computed and are presented in Tables 1–3. Furthermore, the results were compared with the USEPA (1986) and the NESREA (2011) surface water discharge limits.

The percentage pollutant removal efficiency $\boldsymbol{T_\varepsilon}$ of a particular filter system with respect to any particular parameter as given by Ataguba & Brink (2020) is stated below:

$$\boldsymbol{T_\varepsilon}(\boldsymbol{x})\% = \frac{\boldsymbol{C_d} - \boldsymbol{C_x}}{\boldsymbol{C_d}} \times 100$$

$\boldsymbol{C_d}$ = Concentration of parameter in influent (pre-filtration, untreated)

$\boldsymbol{C_x}$ = Concentration of parameter in the effluent (post-filtration) x

The average metals removal efficiency equals the average of all the $\boldsymbol{T_\varepsilon}(\boldsymbol{x})$ for individual filter systems from all the automobile workshops.

RESULTS AND DISCUSSION

The average metals concentrations in stormwater runoff samples before (untreated) and after filtration, from five automobile workshops, using the different filter media are presented in Figures 2–5. Additionally, Tables 2–4 show the average filtered metals concentrations and percentage removal efficiencies for the different filtration media. Figure 6 and Table 5 show individual average metal removal efficiencies with respect to individual filter systems and metals. The overall performance of each filter system is presented in Figure 7 and Table 6.

GAC-RH percentage removal efficiency

The GAC-RH combined filter media showed the best overall metals percentage removal efficiency with an average combined metals removal of around 61%. Consideration of metals removals individually yielded the following notable results: Cadmium: The concentration of untreated samples ranged between 0.014–0.042 mg/L and reduced to range 0.006–0.018 mg/L (Figure 2). The GAC-RH combination showed the highest average percentage removal of cadmium at 46% (Figure 6 and Table 5). Copper: The concentration of untreated samples ranged between 0.021–0.04 mg/L and was reduced to range 0.006–0.012 mg/L (Figure 3). The GAC-RH combination showed the lowest average percentage removal of copper at 64% (Figure 6 and Table 5). Lead: The concentration of untreated samples ranged

Table 2 | Average metals concentrations in filtered and untreated samples and percentage removal efficiencies in automobile workshops 1 and 2

	Workshop 1							**Workshop 2**						
Metals (mg/L)	**GAC-RH**	**T_e(GAC-RH)%**	**GR-GAC**	**T_e(GR-GAC)%**	**RH-only**	**T_e(RH-only)%**	**Untreated**	**GAC-RH**	**T_e(GAC-RH)%**	**GR-GAC**	**T_e(GR-GAC)%**	**RH-only**	**T_e(RH-only)%**	**Untreated**
Cadmium	0.01	52.38	0.01	56.56	0.02	14.55	0.021	0.017	23.10	0.018	21.32	0.021	6.30	0.022
Copper	0.006	73.33	<MDL	≈100	<MDL	≈100	0.023	0.010	52.00	<MDL	≈100	<MDL	≈100	0.021
Lead	0.086	92.67	0.18	84.54	0.050	95.78	1.17	0.19	77.34	0.43	49.28	0.14	83.82	0.85
Iron	12.3	67.60	23.48	38.15	26.13	31.17	37.96	11.91	66.34	18.68	47.20	25.16	28.90	35.38

Note: <MDL = Less than method detection limit.

Table 3 | Average metals concentrations in filtered and untreated samples and percentage removal efficiencies in automobile workshops 3 and 4

	Workshop 3							**Workshop 4**						
Metals (mg/L)	**GAC-RH**	**T_e(GAC-RH)%**	**GR-GAC**	**T_e(GR-GAC)%**	**RH-only**	**T_e(RH-only)%**	**Untreated**	**GAC-RH**	**T_e(GAC-RH)%**	**GR-GAC**	**T_e(GR-GAC)%**	**RH-only**	**T_e(RH-only)%**	**Untreated**
Cadmium	0.006	54.62	0.007	52.61	0.015	−5.62	0.014	0.014	42.73	0.017	32.60	0.024	6.61	0.025
Copper	0.012	71.35	0.015	62.81	0.015	63.91	0.040	0.012	61.32	0.015	53.31	0.016	49.83	0.032
Lead	0.094	68.40	0.18	40.50	0.052	82.45	0.30	0.70	47.49	0.89	33.36	0.85	36.20	1.33
Iron	9.78	70.07	16.80	48.60	21.24	35.03	32.69	14.33	60.84	21.46	41.37	25.42	30.55	36.59

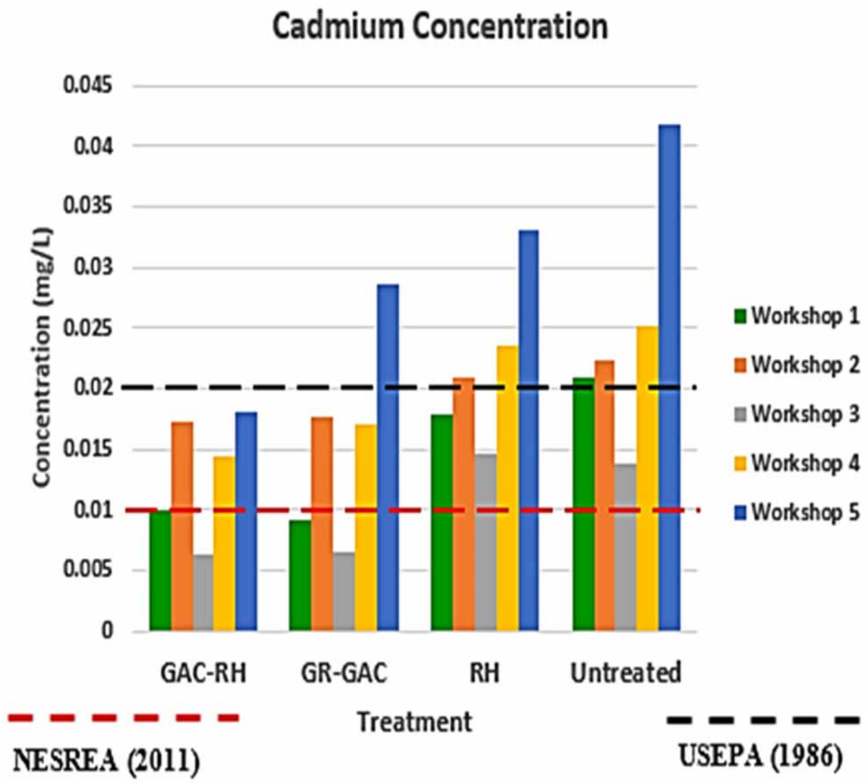

Figure 2 | Filtered and untreated cadmium concentrations.

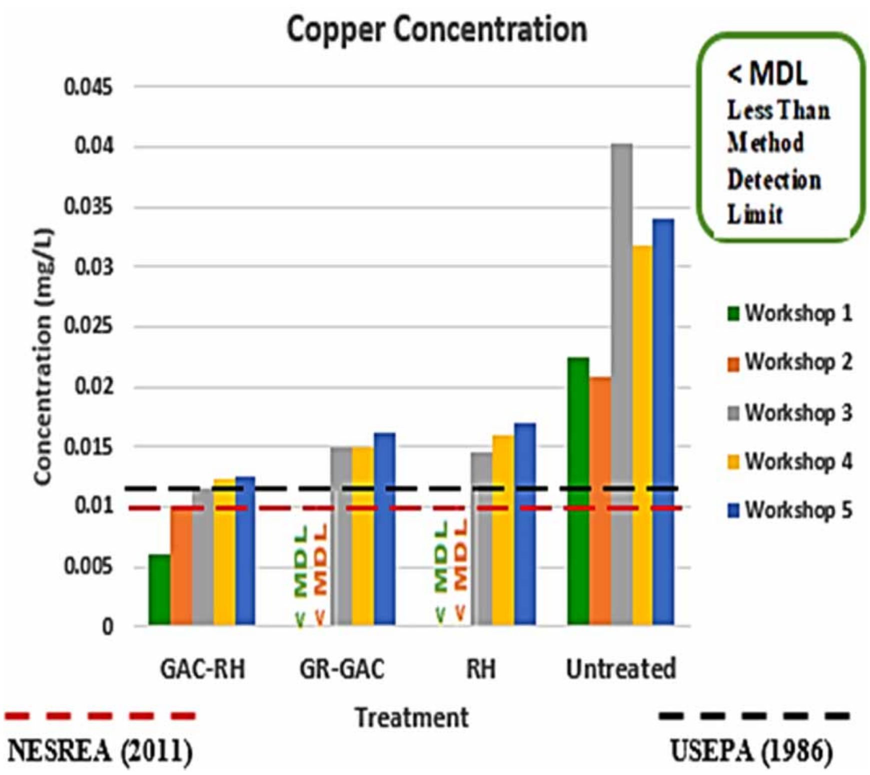

Figure 3 | Filtered and untreated copper concentrations.

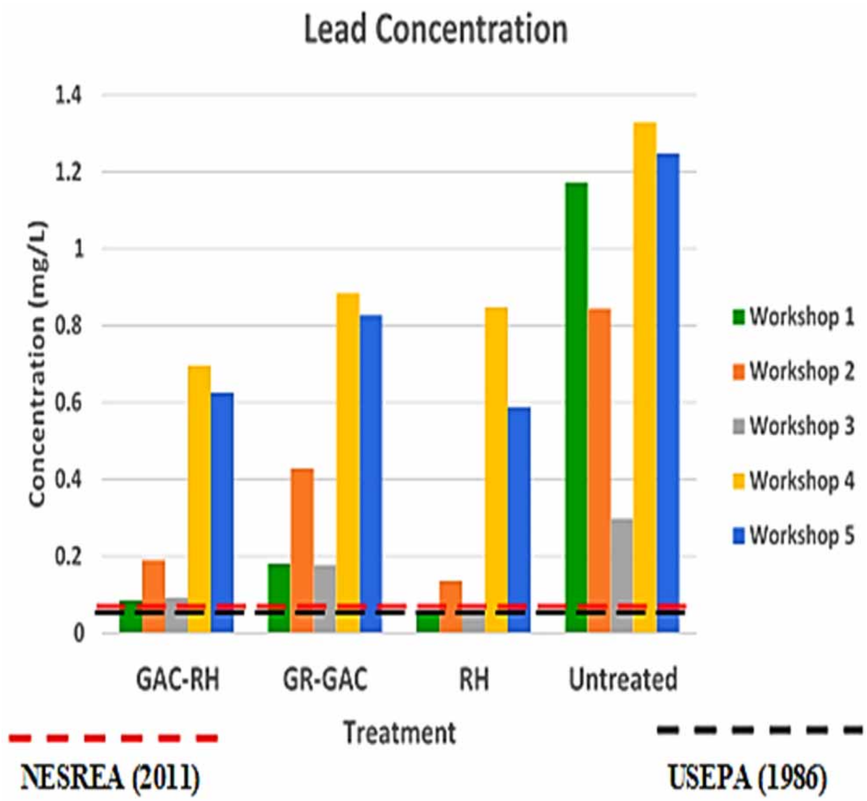

Figure 4 | Filtered and untreated lead concentrations.

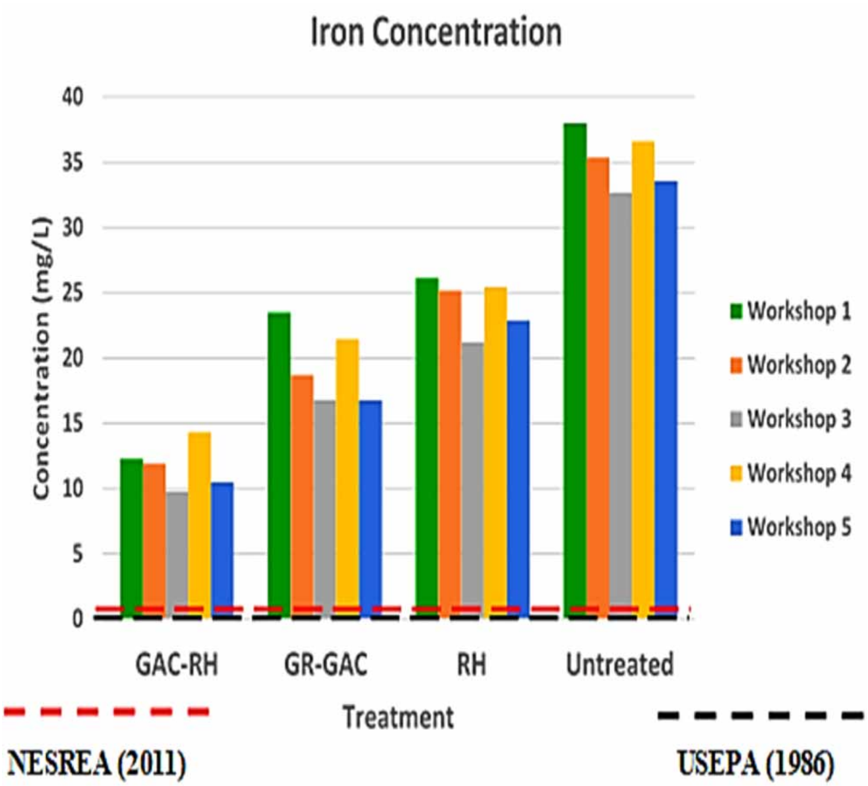

Figure 5 | Filtered and untreated Iron concentrations.

Table 4 | Average metals concentrations in filtered and untreated samples and percentage removal efficiencies in automobile workshop 5

	Workshop 5						
Metals (mg/L)	GAC-RH	T_e(GAC-RH)%	GR-GAC	T_e(GR-GAC)%	RH-only	T_e(RH-only)%	Untreated
Cadmium	0.018	57.03	0.029	31.57	0.033	20.96	0.042
Copper	0.012	63.52	0.016	52.44	0.017	50.16	0.034
Lead	0.63	49.91	0.83	33.66	0.59	52.81	1.25
Iron	10.50	68.75	16.75	50.15	22.89	31.86	33.59

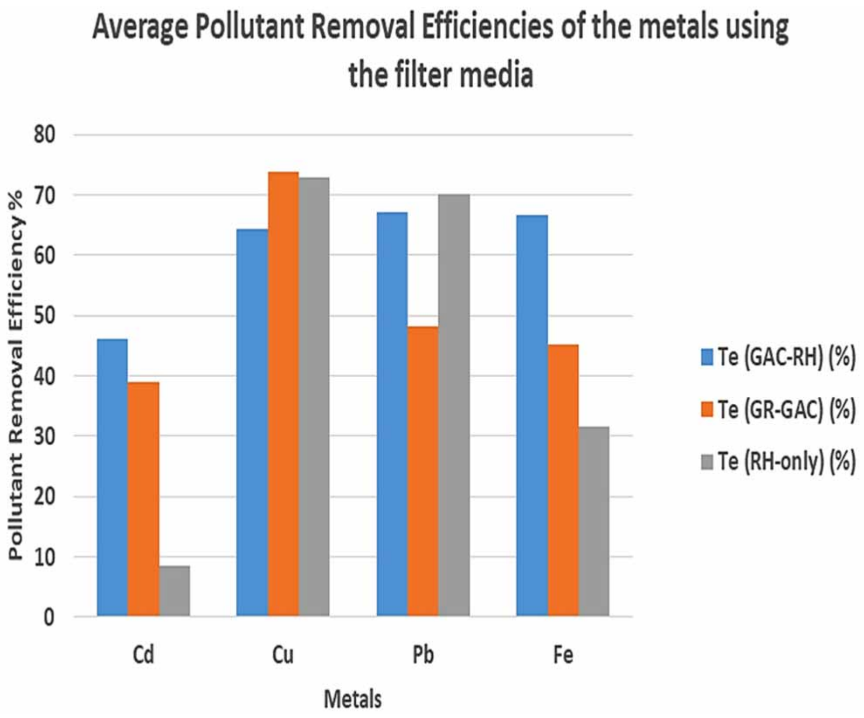

Figure 6 | Pollutant removal efficiency of the filters.

Table 5 | Individual average workshop metal percentage removal efficiencies

	T_e (GAC-RH) (%)				T_e (GR-GAC) (%)				T_e (RH-only) (%)			
Workshop	Cd	Cu	Pb	Fe	Cd	Cu	Pb	Fe	Cd	Cu	Pb	Fe
1	52.4	73.3	92.7	67.6	56.6	≈100	84.5	38.2	14.6	≈100	95.8	31.2
2	23.1	52.0	77.3	66.3	21.3	≈100	49.3	47.2	6.30	≈100	83.8	28.9
3	54.6	71.4	68.4	70.1	52.6	62.8	40.5	48.6	−5.6	63.9	82.5	35.0
4	42.7	61.3	47.5	60.8	32.6	53.3	33.4	41.4	6.6	49.8	36.2	30.6
5	57.0	63.5	49.9	68.8	31.6	52.4	33.7	50.1	21.0.	50.2	52.8	31.9
Average	46.0	64.3	67.2	66.7	38.9	73.7	48.3	45.1	8.6	72.8	70.2	31.5

between 0.30–1.33 mg/L and was reduced to 0.08–0.7 mg/L (Figure 4). The average lead removal efficiency was 67% (Figure 6 and Table 5), close to the highest lead removal efficiency of 70% by the RH-only filter. Iron: The concentration of unfiltered samples ranged between 32.6–38 mg/L and was reduced to 9.7–14.4 mg/L (Figure 5). Reduction of

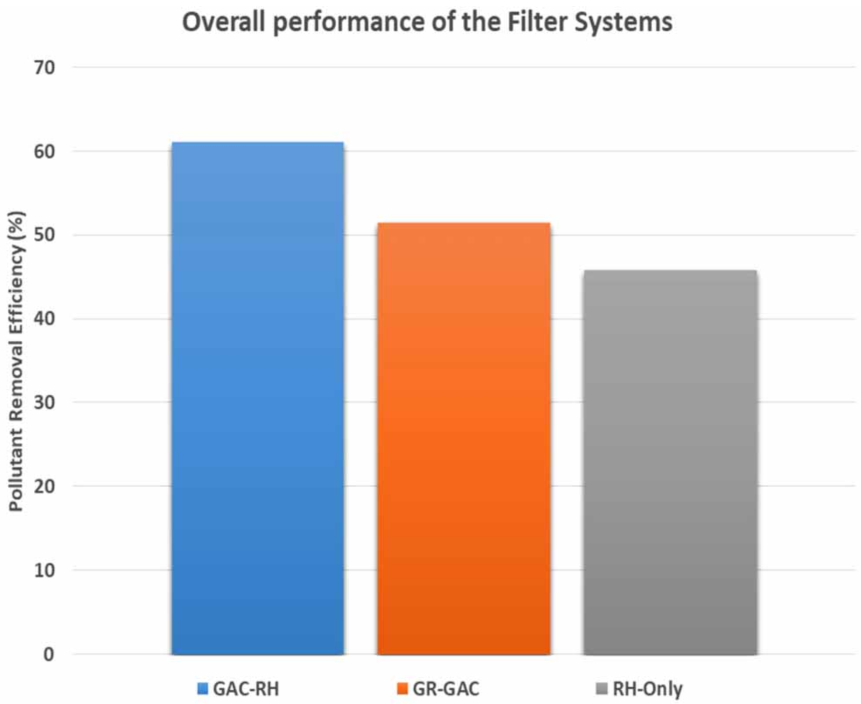

Figure 7 | Performance of the three filter systems.

Table 6 | Overall performance of the filter systems

	T_e(GAC-RH)	T_e(GR-GAC)	T_e(RH-only)
Average metals removal efficiency (%)	61.1	51.5	45.8
Rank	*1*	*2*	*3*

iron concentration by the GAC-RH filter was notably higher than that of the other filter media (67% compared to GR-GAC filter 45% and RH only 32%).

GR-GAC percentage removal efficiency

The GR-GAC combined filter media showed the second best overall metals percentage removal efficiency with an average combined metals removal of around 52%. Consideration of metals removals individually yielded the following notable results: Cadmium: The concentration of untreated samples ranged between 0.014–0.042 mg/L and reduced to the range 0.007–0.029 mg/L (Figure 2). The filter combination showed the second highest average cadmium removal at 39% (Figure 6 and Table 5). Copper: The concentration of untreated samples ranged between 0.021 and 0.04 mg/L and reduced to range <MDL–0.016 mg/L (Figure 3). The GR-GAC had the highest average copper percentage removal at around 74%. This was similar to the removal recorded for the RH-only filter (73%) and notably higher than the removal for the GAC-RH combination (64%) (Figure 6 and Table 5). Lead: The concentration of untreated samples ranged between 0.30 and 1.33 mg/L which reduced to the range 0.18–0.89 mg/L (Figure 4). This filter had the lowest average lead percentage removal (48%), which was notably lower than the other filter media (GAC-RH at 67% and RH-only at 70%). Iron: The concentration of untreated samples ranged between 32.6 and 38 mg/L, which reduced to 16.7–23.5 mg/L (Figure 5). The average removal was second highest at 45% (Figure 6 and Table 5).

RH-only percentage removal efficiency

The RH-only filter media showed the lowest overall metals percentage removal efficiency with an average combined metals removal of around 46%. Consideration of metals removals individually yielded the following notable results: Cadmium: The concentration of untreated samples ranged between 0.014 and 0.042 mg/L, which reduced to 0.015–0.033 mg/L (Figure 2). The RH-only filter had the lowest average cadmium removal at around 9% as well as a negative removal recorded in one case, indicating that the material may add cadmium to the water (Figure 6 and Table 5). Copper: The concentration on untreated samples ranged between 0.021 and 0.04 mg/L and reduced to between <MDL and 0.017 mg/L (Figure 3). As stated above, the average copper removal was similar to the removal recorded for the GR-GAC filter at 73% (Figure 6 and Table 5). Lead: The concentration of untreated samples ranged between 0.30 and 1.33 mg/L and reduced to range 0.05–0.85 mg/L (Figure 4). The RH-only filter showed the best average lead removal at 70% (Figure 6 and Table 5). Iron: The concentration of untreated samples ranged between 32.6 and 38 mg/L and reduced to range 21.2–26.2 mg/L. The average iron removal was low at 32% (Figure 6 and Table 5).

Consideration of metals removal efficiencies separately:

- Cadmium was generally poorly removed by all filter media with a maximum removal of 46% by the GAC-RH combination.
- The RH-only filter had a very low average cadmium removal percentage (9%). Additionally, a negative removal was recorded in one case, indicating that the material may add cadmium to the water. This possibility requires further research.
- Copper was similarly removed by the GR-GAC (74%) and RH-only filters (73%) with the GAC-RH filter showing the lowest removal (64%). Additionally, nearly 100% removals were found in some cases for the first two combinations, indicating that they can be very effective at copper removal.
- The GAC-RH filter had the lowest average lead percentage removal (48%), which was notably lower than the other filter media (GAC-RH at 67% and RH-only at 70%).
- Iron percentage removals were notably higher for the GAC-RH combination when compared to the other filter media (67% compared to GR-GAC at 45% and RH-only at 32%).

Comparison of treated sample concentrations with Nigerian and USEPA discharge limits for surface waters

Consideration of the treated samples in comparison with NESREA (2011) and USEPA (1986) discharge limits showed varying results, for example, cadmium concentrations for automobile workshops 1 and 3 generally met both the Nigerian and USEPA limits for GAC-RH and GR-GAC filter media. However, the concentrations for automobile workshops 2 and 4 generally met only the USEPA limits for GAC-RH and GR-GAC filter media while automobile workshop 5 only met once the USEPA limit (Figure 2). Copper was reduced close to discharge limits but did not meet them in most cases (Figure 3). Similarly, lead concentrations also only met discharge limits in a few cases (Figure 4). Iron concentrations were far above discharge limits in all cases. The results therefore show that stormwater runoff from automobile workshops were heavily polluted with metals, with possible dire consequences for receiving waters. Therefore, further research into reduction of said metal pollutions is of the utmost importance.

Comparison of results with other research

All the filters reduced the metals concentrations. The percentage removal of cadmium was the lowest for all filters. López-Mesas *et al.* (2011) has attributed the low percentage removal of cadmium to a 'clear competition' among the metals as a result of lower adsorption of the cadmium by the biomaterial filter used for the bio-separation of Pb and Cd from aqueous solution. The researchers used cork waste, which is a biomaterial, to separate lead and cadmium from aqueous solution. The study showed that agricultural as well as biomaterial waste can be used as low cost filter materials for heavy metals removal in polluted water.

Combined filters, GAC-RH and GR-GAC produced overall 61% and 52% average metals removal, respectively, while the RH-only filter produced an overall 46% average metals removal efficiency (Figure 7 and Table 6). This tentatively indicates that a combination of filter materials may promote higher efficiency of pollutants removal as was found by Reddy *et al.* (2014) and Abu-El-Halawa & Zabin (2017).

The removal of the individual metals from the stormwater samples varied significantly depending on the properties of the metal, the concentration of the metals and the filter materials as was also found by Reddy *et al.* (2014). Some reductions were successful and below discharge limits. However, the varied results indicate that reductions cannot be guaranteed and this is important since discharging stormwater runoff with high concentration of metals from automobile workshops into receiving surface water can be detrimental to the health of the receiving water source (Jaishankar *et al.* 2014; Shah 2017).

Further treatment, possibly through further filtration, would be required to lower the concentrations of the studied metals to ensure effluent of the required standard. This further filtration could be achieved by implementing low cost modifications of these filter materials using oxidizing agent, organic/mineral acids, bases and even combinations of absorbents (Renu *et al.* 2017). Increasing/decreasing the depth of these filter materials does not affect the efficiency of metal removal since the metal uptake by the filter media occurs mainly about 5 cm depth of the surface of the filter (Hatt *et al.* 2007b; Lim *et al.* 2015).

Researchers have shown that the adsorption capacity of heavy metals by RH increased with modification of the adsorbent when compared with unmodified adsorbent. Kumar & Bandyopadhyay (2006) reported that the adsorption capacity of cadmium increased from 8.58 mg/g using unmodified RH to 20.24 mg/g with sodium hydroxide modified RH. In comparison with this research, the pollutant removal efficiency of cadmium using RH-only filter increased from 8.6% to 46% with combined GAC-RH filter. Similarly, it has been reported that the adsorption capacity of lead increased from 4.23 mg/g using unmodified RH to 108 mg/g with tartaric modified RH (Wong *et al.* 2003; Tarley & Arruda 2004). However, comparing pollutant removal efficiency of RH-only with GAC-RH for lead, there is a slight decrease in the removal efficiency from 70.2% to 67.2% using these respective filters. This may imply that the efficiency of GAC-RH to remove lead can be greatly improved by chemical modification of the RH component of the combined filter.

Granular activated carbon which is an engineered adsorbent, is a modified form of carbon with high surface area in the range of 10^2 and 10^3 m^2/g and high porosity which allows for high adsorption capacity (Worch 2012). The results obtained from this research (Table 6) showed that GAC-RH combined filter system performed better in heavy metals removal efficiency of about 1.2 times that of GR-GAC combined filter system and about 1.34 times that of RH-only filter system. This showed that physical modification of filter materials by way of combining filters can improve the performance of the filter systems. Similarly, Monser & Adhoum (2002) has also reported that chemically modified granular activated carbon performed better in removing heavy metals four times that of granular activated carbon not chemically modified.

From the study areas, the average cost of purchasing carbon produced from wood combustion and processing same into GAC via pyrolysis was 150 USD per tonne. However, the cost of procuring RH was practically free as it is generally waste product from rice milling that needed to be disposed. The cost of river gravel was 65 USD per tonne.

CONCLUSIONS

The results obtained from this study were generally varied. It must be noted that use of local low cost materials brings an inherent variation in standards with the result that percentage metals removals may differ not only due to variations in filter material media, but also due to variations in the filter material local sources. However, the following notable trends were found:

- All tested filters, viz. GAC-RH, GR-GAC and RH-only removed metals from automobile workshop stormwater runoff. However, the percentage metals removals varied between filters indicating that the application of specific filter media required to accomplish utmost removal of specific metal is necessary. For example, the GAC-RH combination performed best overall with average removal efficiency >60% and can therefore be considered for general metals removal application, The GR-GAC combination (with overall average removal efficiency of >50%) as well as the RH-only filters (with overall average premoval efficiency of >45%) can be considered for targeted removal of copper. The RH-filter (with average lead removal of 70%) can also be considered for targeted removal of lead.
- Comparison of results with NESREA (2011) and USEPA (1986) showed that the automobile workshop stormwater runoff was heavily polluted with the investigated metals, with possible direct consequences for receiving waterbodies. Discharge standards were not often met. This indicates that further research into low cost technology for removal of metals from automobile workshop runoff is not only warranted, but of great importance when considering the natural environment. For example, the potential of other low cost filter materials that are locally available, such as organically modified clay, can be investigated.

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DATA AVAILABILITY STATEMENT

Data cannot be made publicly available; readers should contact the corresponding author for details.

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