

# Application of isotherm models to combined filter systems for the prediction of iron and lead removal from automobile workshop stormwater runoff

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Langmuir and Freundlich isotherm adsorption models were used to predict iron and lead removal from automobile workshop stormwater runoff. Combined low-cost filter systems consisting of granular activated carbon–rice husk (GAC–RH) and river gravel–granular activated carbon (GR–GAC) were used in this study. The effects of adsorbent dosage and contact time on the adsorption capacity of the adsorbents, as well as the removal efficiencies of the adsorbent systems, were also investigated. The results for the Langmuir model generally showed favourable adsorption processes, with all  $R_L$  values  $< 1$  (in the range 0.358–0.518). The Langmuir model gave better predictions for iron and lead removal, with high  $R^2$  values (in the range 0.842–0.969), while the root mean square error (RMSE) values ranged from 0.002 to 2.366. The Freundlich model parameters indicated chemisorption processes with all  $n$  values  $< 1$  (in the range 0.1296–0.4675).  $R^2$  values were in the range of 0.634–0.916 while RMSE values ranged from 0.002 to 0.1765. Additionally, the removal efficiencies for iron and lead using GAC–RH filter system (54% and 48%, respectively) were found to be higher than those obtained using GR–GAC filter system (35% and 25%, respectively). The adsorption capacities of the adsorbents decreased with increased dosages of the adsorbent, with optimum adsorbent dosage of 0.5 g and equilibrium contact time of 80 min for the combined filter adsorbents. Further research towards modifying adsorbents for removal of oil and grease from polluted automobile workshop stormwater runoff are warranted.

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## INTRODUCTION

Stormwater runoff from different land uses in urban areas is a major source of pollution to receiving streams and rivers, which affects the health of receiving water bodies (Laurenson et al., 2013). Therefore, a major goal for stormwater management, with respect to the water quality standards of a receiving water body, is to minimize pollutant loads discharged. This is necessary in order to maintain the natural hydrological patterns of a catchment area as far as possible (NAP, 2009; Argue and Pezzaniti, 2005). Generally, the presence of heavy metals in stormwater/wastewater effluents can be very toxic and harmful to aquatic and terrestrial life when discharged into the environment without any treatment (Kavand et al., 2011). Accumulation of pollutants in a water environment can result from discharging untreated stormwater runoff into an environment that has limited natural purification capacity, with the result that the ecosystem cannot reasonably absorb the pollutants (UNEP, 2004).

Stormwater management has evolved beyond the conventional practice of immediate collection, conveyance and disposal of runoff using grey infrastructures, towards the use of low-cost and low-impact development (LID) technologies. These are less expensive technologies that collect, detain and gradually release the runoff for groundwater recharge or final disposal into the receiving water body. According to Guyer (2017), LID is a land planning or engineering strategy aimed at maintaining or restoring the natural hydrology of any catchment for the protection of the natural resources of the site towards achieving the goal of environmental regulatory requirements.

The removal of heavy metals from stormwater or wastewater via adsorption have been achieved in past studies using un-combined filter systems of granular activated carbon (GAC) as well as other low-cost agricultural wastes (Khan et al., 2004; Desta 2013). These technologies, however, required further effluent treatment to meet discharge standards (Reddy et al., 2014; Larm and Wahlsten, 2018; Wang et al., 2017). Ataguba and Brink (2021) therefore investigated and developed combined filter systems that use low-cost locally available materials specifically for application to water quality improvement of polluted stormwater runoff from automobile workshops in Nigeria. This became necessary as the application of conventional iron and lead removal technologies such as ultra-filtration, electro dialysis, ion exchange, chemical precipitation, reverse osmosis, etc., in developing countries have been reported to be uneconomical and technically cumbersome, due to the high cost of operation as well as non-availability of required labour (Brown et al., 2000; Fu and Wang, 2011; Bahgat et al., 1999).

Adsorption, in the treatment of polluted water, has been referred to as a surface process where ions or molecules of the pollutants are removed from the water and attached to the surface of a solid or adsorbent (Piccin et al., 2017; Agunwamba, 2001). Adsorption using activated carbon has been in use for treatment of drinking water for over 100 years and has proved to be efficient in the removal of adsorbates in water (Worch, 2021). According to Worch (2021), there are two types of adsorption, namely, physisorption (physical adsorption) and chemisorption (chemical adsorption). While physisorption results from Van der Waal's forces, chemisorption is caused by a chemical reaction between the adsorbate and the surrounding surface of the adsorbent.

Stormwater treatment models can be designed to predict the performance of proposed stormwater treatment processes and technologies subjected to varying conditions with the overall aim of protecting receiving water bodies from pollution (Wong et al., 2006). One aim of characterizing and modelling the pollutants in stormwater runoff is to develop suitable options that can lower the concentrations of pollutants or minimize runoff volume, culminating in the overall reduction in the pollutant load that is received by the streams or rivers (Charters, 2016).

Several adsorption isotherm models have been developed and used to describe the behaviour of adsorbate on adsorbent materials in the past. Some of these models are presented in Table 1. The terms in the equations have been defined in the different sources cited from.

Adsorption isotherm models are functions that relate the change in the quantity of adsorbate adsorbed on the surface of the adsorbents, and the quantity of adsorbate left in liquid phase under equilibrium, with respect to variation in pressure at constant temperature (Piccin et al., 2017). Linear forms of the Langmuir and Freundlich isotherm models have been successfully used to describe the adsorption of ions from single and mixed metal solutions onto soils or other natural adsorbents under constant temperature (Echeverría et al., 1998; Christophi and Axe, 2000; Gulbaz et al., 2015; Song and Liu, 2013; Thuy Chung et al., 2015; Wu et al., 2014). It has been reported in literature that Langmuir and Freundlich isotherm models are optimum adsorption models when compared to others such as Temkin, Sips, Hill-Deboer, etc. (Wang and Guo, 2020; Zhuang et al., 2020; Manaa et al., 2020). The Langmuir and Freundlich models are frequently used due to the simplicity of their application in linear regression modelling (Wang and Guo, 2020). These models were therefore selected for further investigation in this research.

The use of only the coefficient of determination,  $R^2$ , to describe the suitability/fitness of isotherm models in describing an adsorption process has been reported to be insufficient, since this parameter considers the difference between the theoretical and experimental data in linear plots (Hami et al., 2021). Appropriate isotherm models to describe adsorption can be determined by using error functions to validate the linearized isotherm equations with experimental results (Hami et al., 2021; Balarak and Salari, 2019). Optimal adsorption isotherm models are generally characterized by high  $R^2$  values and low values of error functions. Common error functions that have been used by researchers include: residual sum of squares (RSS), sum of absolute errors (SAE), hybrid function fractional error (Hybrid), average relative error (ARE), non-linear chi-square test ( $\chi^2$ ), root mean square error (RMSE) among others (Hami et al., 2021, Amtul et al., 2017).

This paper reports on the modelling of adsorption of iron and lead from automobile workshop stormwater using Langmuir and Freundlich isotherm models. The aims of the study were:

- To predict the removal of iron and lead from automobile stormwater runoff onto combined filters of GAC–RH and GR–GAC as well as to determine the fit of the predicted data to the isotherm models, using the model parameters and error functions
- To determine the effect of adsorbent (GAC–RH and GR–GAC) dosage on the adsorption capacities of the adsorbents for the removal of iron and lead from automobile stormwater runoff
- To determine the adsorbent removal efficiencies for removal of iron and lead from automobile stormwater runoff
- To determine the effect of contact time on the efficiencies of iron and lead removal using GAC–RH and GR–GAC combined filters

**Table 1.** Common isotherm models (See Ayawei et al., 2017)

Model	Governing equation	Reference
Henry's isotherm	$q_e = K_{HE} C_e$	Fost and Aly (1981)
Hill-Deboer isotherm	$\ln \left[ \frac{C_e(1-\theta)}{\theta} \right] - \frac{\theta}{1-\theta} = -\ln K_1 - \frac{K_2 \theta}{RT}$	Kumar et al. (2011)
Fowler-Guggenheim model	$\ln \left[ \frac{C_e(1-\theta)}{\theta} \right] = -\ln K_{FG} + \frac{2\omega\theta}{RT}$	Dabrowski (2001)
Langmuir isotherm	$\frac{1}{Q_e} = \left[ \frac{1}{Q_m K_L} \right] \frac{1}{C_e} + \frac{1}{Q_m}$	Ayawei et al. (2017)
Freundlich isotherm	$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e$	Ayawei et al. (2017)
Temkin isotherm	$Q_e = \frac{Rt}{b} \ln K_T + \frac{Rt}{b} \ln C_e$	Vijayaraghavan et al. (2006)
Jovanovic isotherm	$\ln Q_e = \ln Q_{max} - K_J C_e$	Kiseler (1958)
Sips isotherm	$\beta_s \ln C_e = -\ln \left( \frac{K_s}{q_e} \right) + \ln(a_s)$	Elmorsi (2011)
Toth isotherm	$\ln \frac{q_e^n}{q_m^n - q_e^n} = n \ln K_L + n \ln C_e$	Podder and Majumder (2016)
Elovich isotherm	$\ln \frac{q_e}{C_e} = \ln K_e q_m - \frac{q_e}{q_m}$	Kumar et al. (2011)

The use of these low-cost combined adsorbents as combined filters and the use of these isotherm models to predict iron and lead adsorption from automobile workshop stormwater, along with the metals' effect on quality of urban runoff, have hitherto been neglected, and are the major novel contributions of this study.

## MATERIALS AND METHODS

Figure 1 shows the adsorption mechanism. The selected adsorbents on which the adsorption took place were granular activated carbon (GAC), rice husk (RH) and river gravel (RG). Iron and lead were the adsorbates. The reverse of this process, called desorption, was not however carried out in this research. The combined GAC–RH and GR–GAC filter systems were modelled as a series of compartments by using theoretical removal mechanisms for each compartment, as shown in Fig. 1. The compartments were modelled as sites/aspects of the adsorptive filtration processes.

The concentrations retained in the adsorbent phase ( $Q_e$ ) were determined using:

$$Q_e = \frac{(C_o - C_e)}{M} \times V \quad (1)$$

$$q_e[\text{GAC}] = \frac{(C_o - C_e)}{m_{\text{GAC}}} \times V_{\text{aq}} \quad (2)$$

$$q_e[\text{RH}] = \frac{(C_o - C_e)}{m_{\text{RH}}} \times V_{\text{aq}} \quad (3)$$

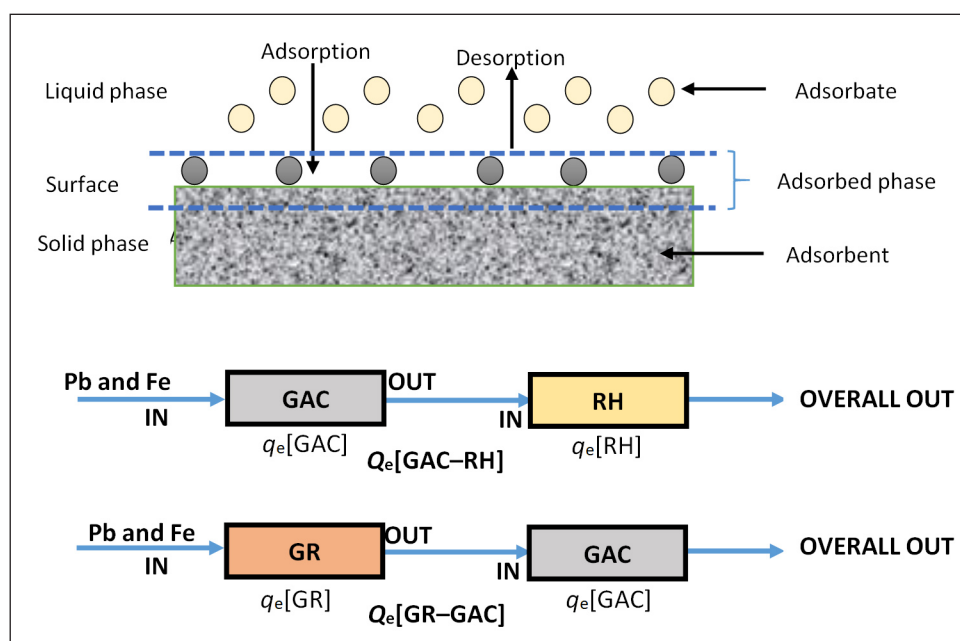
$$q_e[\text{GR}] = \frac{(C_o - C_e)}{m_{\text{GR}}} \times V_{\text{aq}} \quad (4)$$

where  $q_e[\text{GAC}]$  is the adsorption capacity of GAC adsorbent (mg/g),  $q_e[\text{RH}]$  is the adsorption capacity of RH adsorbent (mg/g),  $q_e[\text{GR}]$  is the adsorption capacity of GR adsorbent (mg/g),  $V_{\text{aq}}$  is the volume of the solution containing metal used (L),  $C_o$  is the influent concentration (mg/L),  $C_e$  is the effluent concentration (mg/L),  $m_{\text{GAC}}$  is the dosage of GAC (g),  $m_{\text{GR}}$  is the dosage of GR (g) and  $m_{\text{RH}}$  is the dosage of RH (g). The model equations for the different filter combinations are shown in Table 2.

Stormwater runoff samples, which served as the adsorbate solutions, were obtained from two selected automobile workshops in Nigeria. The characterization of the untreated and treated stormwater runoff samples from the selected automobile workshops has been presented in Ataguba and Brink (2021), along with preparation of the adsorbents used in this research. Laboratory tests were carried out in accordance with APHA (2017) and average values obtained were used for analyses. The laboratory room temperature was maintained at 25°C and the initial average stormwater pH was 9.56. Also the initial concentrations of the adsorbate, iron and lead, were noted as 35.5 mg/L and 1.65 mg/L, respectively. No thermodynamic study was carried out. Adsorbent dosage and contact time effects on the adsorptive removal of iron and lead on prepared GAC–RH and GR–GAC filter beds were tested as batch sorption experiments in a series of capped 250 mL Erlenmeyer flasks at room temperature of 25±1°C with adsorbent dosage range of 0.5 g to 8.0 g. The detailed experimental procedure for adsorption equilibrium determination has been described in Worch (2021). The adsorption capacities of each adsorbent combination at equilibrium were mathematically analysed using Eqs 1–4 and Table 2. This was performed for the different adsorbent dosages. Briefly, the adsorbents were prepared as crushed granular activated carbon, rice husk and gravel samples to allow accommodation in flasks. Suspensions were magnetically agitated at constant speed (200 r/min) until equilibrium was reached. The process was repeated for the different adsorbent dosages as mentioned above and contact time in the range of 5–80 min. After equilibrium was attained, the resulting solutions were centrifuged at 4 000 r/min and the supernatant analysed using ICE 3000 Series AA Spectrometer (flame atomic absorption spectrometry technique). All tests were performed in the Water Quality Laboratory at the National Geosciences Research Laboratories in Kaduna, Nigeria.

**Table 2.** Model equation combinations for the different filter combinations

Filter combinations	Equation combinations
GAC + RH	Equation 2 + Equation 3
GR + GAC	Equation 4 + Equation 2



**Figure 1.** Schematic of the adsorption mechanism and modelled compartments

The Langmuir isotherms were obtained from the plot of  $\frac{1}{Q_e}$  vs  $\frac{1}{C_e}$  with a linearized equation:

$$\frac{1}{Q_e} = \frac{1}{b \times Q_m} \left( \frac{1}{C_e} \right) + \frac{1}{Q_m} \quad (5)$$

Similarly, the Freundlich isotherms were obtained from the plot of  $\ln(Q_e)$  vs  $\ln(C_e)$  with a linearized equation:

$$\ln(Q_e) = \left( \frac{1}{n} \right) \times \ln(C_e) + \ln K_F \quad (6)$$

where  $Q_m$  = maximum adsorption capacity (mg/g),  $b$  = constant related to affinity of binding sites (L/mg),  $K_F$  = Freundlich isotherm constant related to the adsorption capacity (mg/g),  $n$  = Freundlich isotherm constant related to the adsorption intensity (L/g)

The concentrations  $C_o$  and  $C_e$  at the optimum adsorbent dosage were used to compute the removal efficiencies for the adsorbents given by Eq. 7.

$$R_E (\%) = \frac{C_o - C_e}{C_o} \times 100 \quad (7)$$

The metal removal efficiencies,  $R_E$ , were used to evaluate the performance of the adsorption processes using the two different combined adsorbents (filters). The study also sought to establish the relationship between the dosages of the different adsorbents and their modelled adsorption capacities, as shown in Figs 10 and 11. Also, for each contact time, the metal removal efficiencies were computed using Eq. 7 and graphs plotted as shown in Figs 12 and 13.

The favourableness/fitness of the predicted data using Langmuir and Freundlich isotherm models were also determined from the equilibrium parameters  $R_L$  and  $n$ , respectively. For Langmuir, the Langmuir isotherm constant related to the adsorption capacity

in mg/g  $R_L = \frac{1}{1+bC_o}$  while Freundlich constants  $n$  and  $K_F$  were obtained from the slope and intercept of  $\ln Q_e$  vs  $\ln C_e$  plots. The nature of the adsorption process based on the Langmuir isotherm model is defined by any of the following relationships (Hamzaoui et al., 2018):  $R_L > 1$  (unfavourable),  $R_L = 1$  (linear),  $0 < R_L < 1$  (favourable) or  $R_L = 0$  (irreversible). Similarly, the nature of the adsorption process based on the Freundlich isotherm model (Hamzaoui et al., 2018) is defined as  $n > 1$  (adsorption is a physical process),  $n < 1$  (adsorption is a chemical process or chemisorption) or  $n = 1$  (adsorption is linear).

In this research, two statistical error functions were used in addition to the coefficient of determination ( $R^2$ ) to determine the suitability/fitness of the adsorption isotherm models under consideration. These error functions were the Chi-square test ( $\chi^2$ ) and the RMSE. The error function analyses and the model equations were obtained using Microsoft Excel.

## RESULTS AND DISCUSSION

Figures 2 to 9 show measured and predicted results using the Langmuir and Freundlich isotherms. Model parameters including RMSE, Chi-square test and  $R^2$  values from the analyses of the results have been presented in Table 3.

From the results represented in Figs 2–5, it was observed that the linearized Langmuir and Freundlich models predicted the removal of lead using the GR–GAC treatment system with  $R^2$  values of 0.889 and 0.814, respectively. Iron adsorption prediction for the GR–GAC system had a better fit to experimental data for the Langmuir model than the Freundlich model, with  $R^2$  values of 0.842 vs 0.645, respectively.

Lead adsorption for the GAC–RH system (Figs 6–9) gave  $R^2$  values of 0.862 and 0.634 for the Langmuir and the Freundlich isotherm models, respectively, whereas iron adsorption for the Langmuir and Freundlich isotherm models gave  $R^2$  values of 0.969 and 0.916, respectively.

**Table 3.** Langmuir and Freundlich isotherm model parameters, removal efficiencies for GAC–RH and GR–GAC combined filters

Isotherm model	Metal and $C_o$ (mg/L)	Adsorbent combination	Model equation	$R^2$	$b$ (L/mg)	$q_m$ (mg/g)	$R_L$	$\chi^2$	RMSE	Average removal efficiency (%)
Langmuir	Lead removal 1.65	GAC–RH	$\frac{1}{Q_e} = 150.45 \left( \frac{1}{C_e} \right) - 84.428$	0.862	0.563	0.012	0.518	0.114	0.0118	48.2
		GR–GAC	$\frac{1}{Q_e} = 805.48 \left( \frac{1}{C_e} \right) - 460.78$	0.889	0.564	0.002	0.518	0.007	0.0022	24.5
	Iron removal 35.5	GAC–RH	$\frac{1}{Q_e} = 406.87 \left( \frac{1}{C_e} \right) - 20.572$	0.969	0.051	0.049	0.358	9.544	2.866	53.6
		GR–GAC	$\frac{1}{Q_e} = 562.15 \left( \frac{1}{C_e} \right) - 18.182$	0.842	0.032	0.055	0.466	1.702	0.187	35.0
Isotherm model	Metal and $C_o$ (mg/L)	Adsorbent combination	Model equation	$R^2$	$1/n$	$n$ (L/g)	$K_F$ (mg/g)	$\chi^2$	RMSE	Average removal efficiency (%)
Freundlich	Lead removal 1.65	GAC–RH	$\ln Q_e = 2.1385 \times \ln C_e - 4.0991$	0.634	2.1385	0.4675	0.0166	0.099	0.0114	48.2
		GR–GAC	$\ln Q_e = 4.2064 \times \ln C_e - 6.0798$	0.814	4.2064	0.2378	0.0023	0.0068	0.0022	24.5
	Iron removal 35.5	GAC–RH	$\ln Q_e = 7.7191 \times \ln C_e - 22.874$	0.916	7.7191	0.1296	$1.17 \times 10^{-10}$	0.353	0.1407	53.6
		GR–GAC	$\ln Q_e = 4.9811 \times \ln C_e - 17.331$	0.645	4.9811	0.2007	$2.97 \times 10^{-8}$	1.362	0.1765	35.0

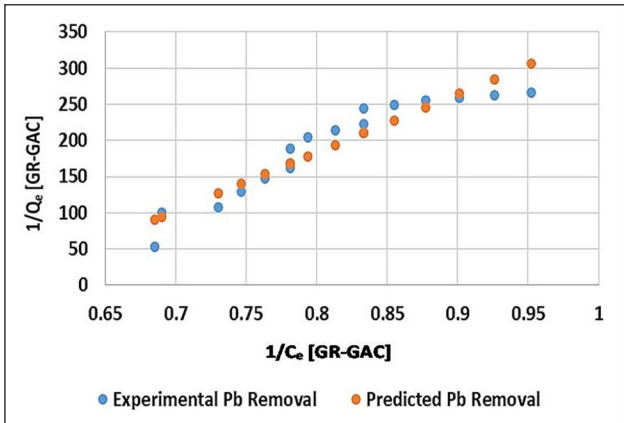


Figure 2. GR-GAC combined filter for lead: Langmuir model ( $R^2 = 0.889$ )

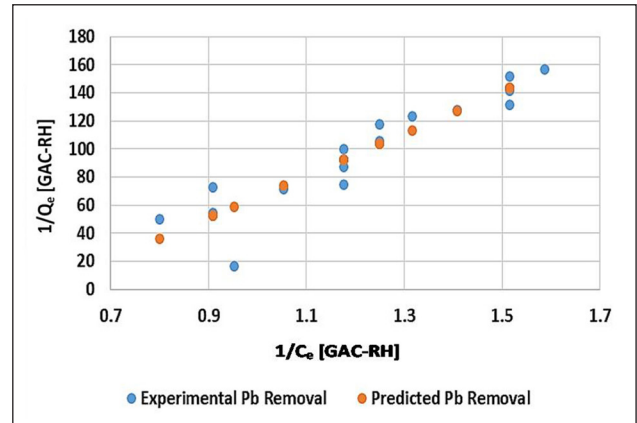


Figure 6. GAC-RH combined filter for lead: Langmuir model ( $R^2 = 0.862$ )

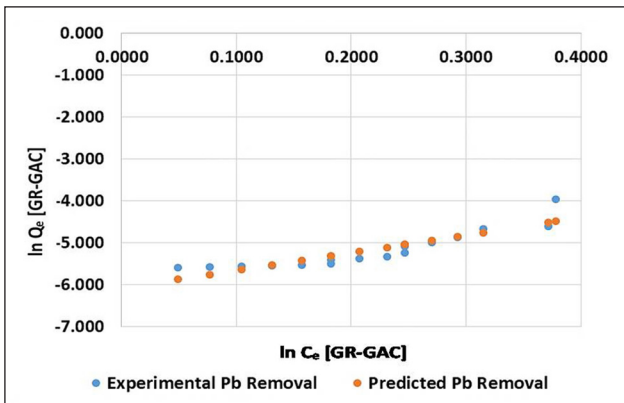


Figure 3. GR-GAC combined filter for lead: Freundlich model ( $R^2 = 0.814$ )

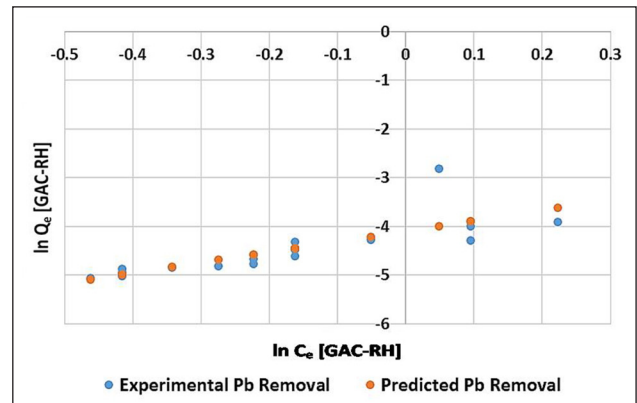


Figure 7. GAC-RH combined filter for lead: Freundlich model ( $R^2 = 0.634$ )

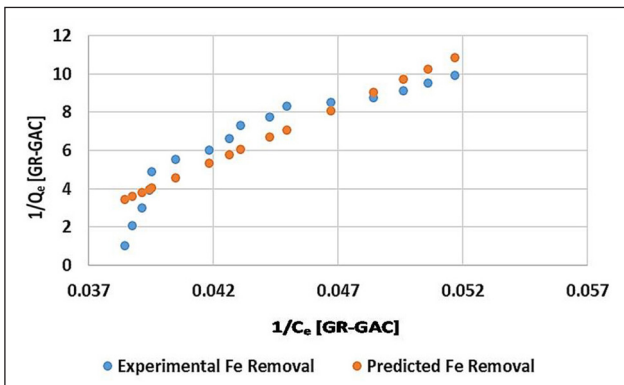


Figure 4. GR-GAC combined filter for iron: Langmuir model ( $R^2 = 0.842$ )

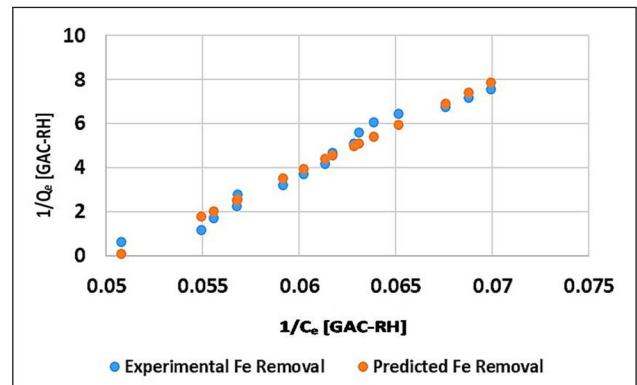


Figure 8. GAC-RH combined filter for iron: Langmuir model ( $R^2 = 0.969$ )

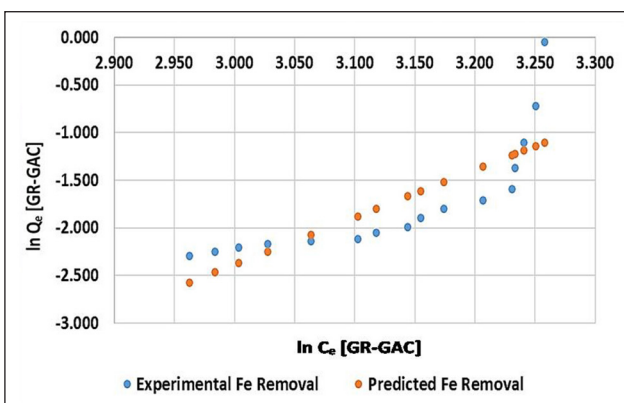


Figure 5. GR-GAC combined filter for iron: Freundlich model ( $R^2 = 0.645$ )

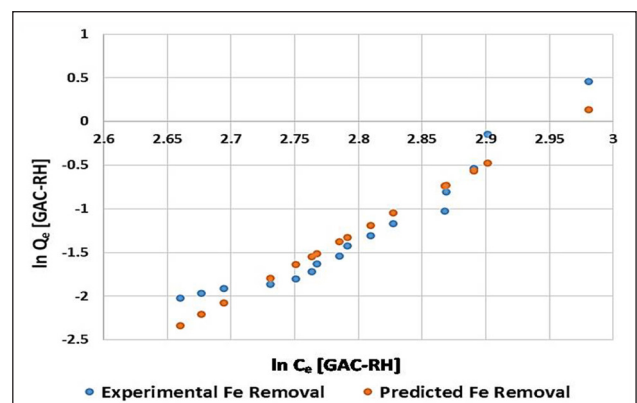


Figure 9. GAC-RH combined filter for iron: Freundlich model ( $R^2 = 0.916$ )



Table 3 summarizes the corresponding Langmuir and Freundlich isotherm parameters, their correlation coefficients ( $R^2$ ) and related chi-square values as well as standard errors for each parameter. Although both models predicted the removal of iron and lead to differing degrees, the Langmuir model consistently gave a better fit to experimental data than the Freundlich model. From the Freundlich isotherm model parameters in Table 3, the adsorption processes were found to be chemisorption as all values of  $n$  were less than 1. Also, the Freundlich isotherm model gave a good fit to measured data with low errors and high  $R^2$ -values. On the other hand, Table 3 showed that the adsorption processes predicted by the Langmuir isotherm were found to be favourable with values of  $R_L$  less than 1; this model also gave a better fit with higher  $R^2$  values and low errors. This trend was also observed by Desta (2013) who found that the Langmuir isotherm model predicted the adsorption of nickel from textile wastewater onto teff straw, with  $R^2 = 0.998$  and  $R_L$  values between 0.298 and 0.986 indicating favourable adsorption, giving a better fit to the data than the Freundlich isotherm model with  $R^2 = 0.748$ , and with  $n$  values ranging between 1 and 10.

### GR-GAC and GAC-RH removal efficiencies

Table 3 shows that the GAC-RH combined filter had percentage concentration removal efficiencies for iron and lead of 53.6% and 48.2%, respectively. The GR-GAC combined filter had lower percentage concentration removals for iron and lead, at 35.0% and 24.5%, respectively. The GAC-RH combined filter therefore performed better in the removal of iron and lead than the GR-GAC combined filter. This result was also reported in Ataguba and Brink (2021) where the systems were tested in real-world applications at automobile workshops in different areas

in Nigeria. Here, the authors reported an average percentage removal efficiency using GAC-RH combined filter of 45.8% for iron and 41.9% for lead. It is presumed that the GAC-RH combined filter gave higher removal efficiencies due to the larger combined surface area (attachment sites) available for adsorption when compared to the GR-GAC combined filter.

### Effect of adsorbent dosage on adsorption capacities

Figures 10 to 13 show the relationships between the modelled adsorption capacity of the adsorbents and the dosage of the adsorbents. From Fig. 10, it was found that the uptake of iron by the GAC-RH filter decreased from 1.6 mg/g to 0.18 mg/g with increase in the dosage of the adsorbents from 0.5 g to 8 g, respectively. This has shown that the optimum dosage of 0.5 g each of GAC and RH resulted in the highest iron uptake, of 1.6 mg/g. Similarly, from Fig. 11, the uptake of lead by the GAC and RH decreased from 0.06 mg/g to 0.008 mg/g with increase in the dosage of the adsorbents from 0.5 g to 8 g, respectively. The optimum dosage of 0.5 g each of GAC and RH resulted in the highest lead uptake, of 0.06 mg/g.

Furthermore, it was found, as shown in Fig. 12, that the uptake of iron by the GR and GAC decreased from 0.98 mg/g to 0.1 mg/g with increase in the dosage of the adsorbents from 0.5 g to 8 g, respectively. This implied that the optimum dosage of 0.5 g each of GR and GAC resulted in the highest iron uptake, of ~1 mg/g. Similarly, from Fig. 13, the uptake of lead by the GR and GAC decreased from 0.019 mg/g to 0.0038 mg/g with increase in the dosage of the adsorbents from 0.5 g to 8 g, respectively. These results showed the optimum dosage of 0.5 g each of GR and GAC which resulted in the highest iron uptake, of ~0.02 mg/g.

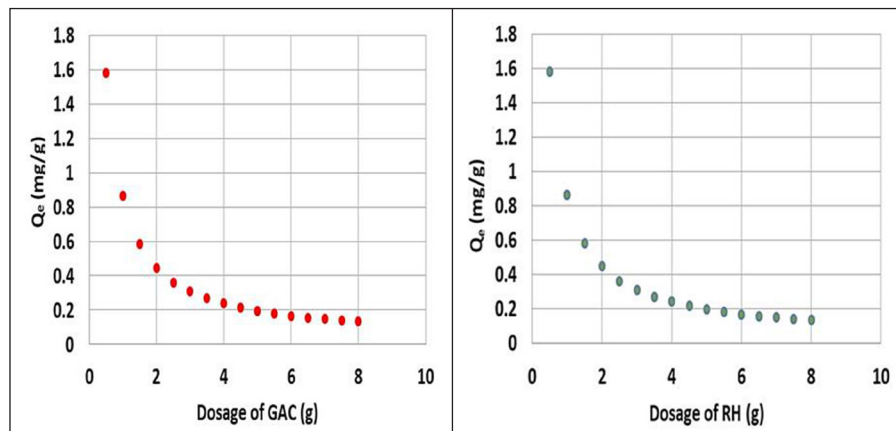


Figure 10. Relationship between the adsorption capacities and dosages of GAC and RH in iron removal using GAC-RH

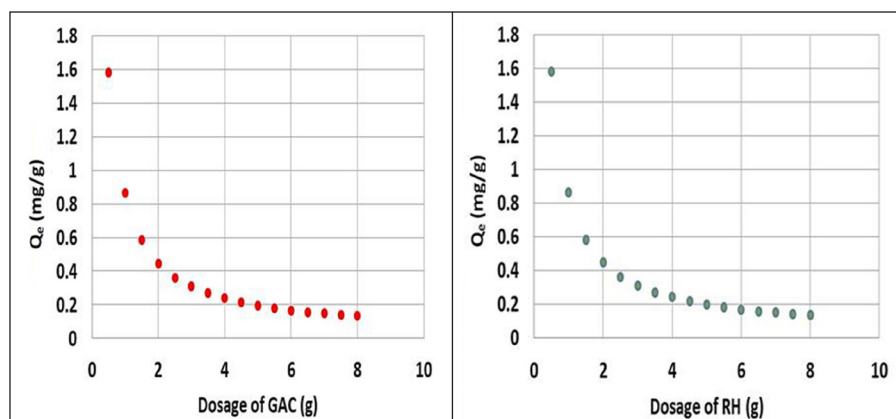


Figure 11. Relationship between the adsorption capacities and dosages of GAC and RH in lead removal using GAC-RH

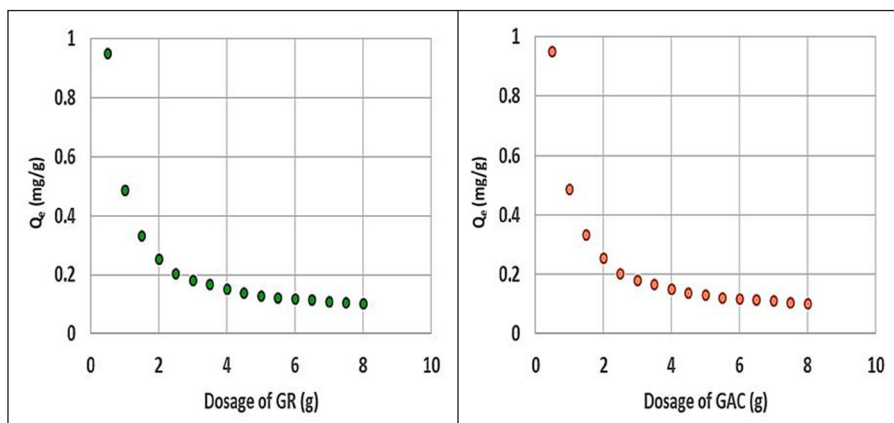


Figure 12. Relationship between the adsorption capacities and dosages of GR and GAC in iron removal using GR–GAC

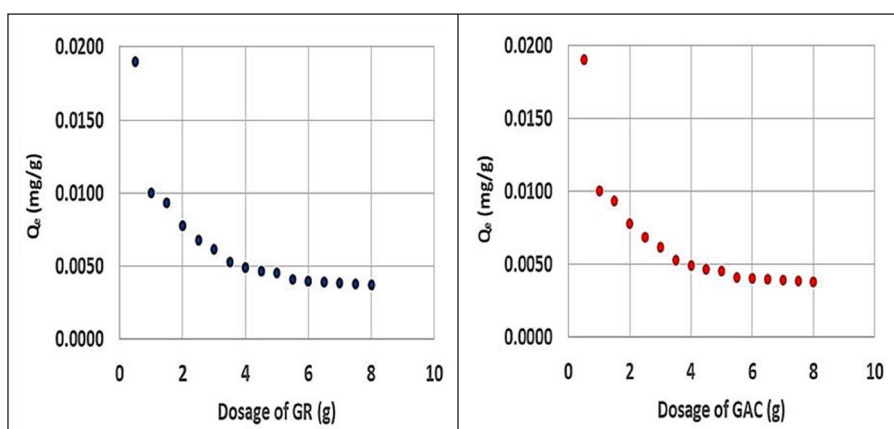


Figure 13. Relationship between the adsorption capacities and dosages of GR and GAC in lead removal using GR–GAC

Some studies reported in the literature have noted a similar trend and have attributed this to an aggregation of adsorbents, which reduced the surface area of the adsorbent available for adsorption to take place (Alghamdi et al., 2019; Radnia et al., 2012; Gorzin and Abadi, 2018).

#### Effect of contact time on the removal efficiency of the metals using the treatment technologies

Figures 14 and 15 show the effect of contact time on the removal efficiency for iron and lead using GAC–RH and GR–GAC treatment technologies, respectively. It can be observed that the two combined filter systems had higher removal efficiency for iron removal than lead removal. The removal efficiency for iron, as shown in Figs 14 and 15, increased steadily with increase in the contact time, from 5 min up to the optimum 80 min, using both GAC–RH and GR–GAC filters. A similar trend was observed in a study by Gorzin and Abadi (2018), where for chromium ion adsorption onto activated carbon the removal efficiency increased up to a contact time of 180 min and then gradually decreased to equilibrium. However, a slight difference noted in the current study was that there was a gradual increase in iron and lead removal up to equilibrium. This difference may be attributed to the fact that combined filter systems were used in this treatment.

The removal efficiency for lead using GR–GAC (Fig. 15) showed a gradual increase with increasing contact time. However, there was a decrease in removal efficiency from 37% to 24% between 5 and 10 min. After this period, a gradual rise in removal efficiency was observed to 80 min of contact time. For the GAC–RH filter in Fig. 14, there was a sharp reduction in removal efficiency from 36% to 24% between contact times of 5–10 min. This may possibly

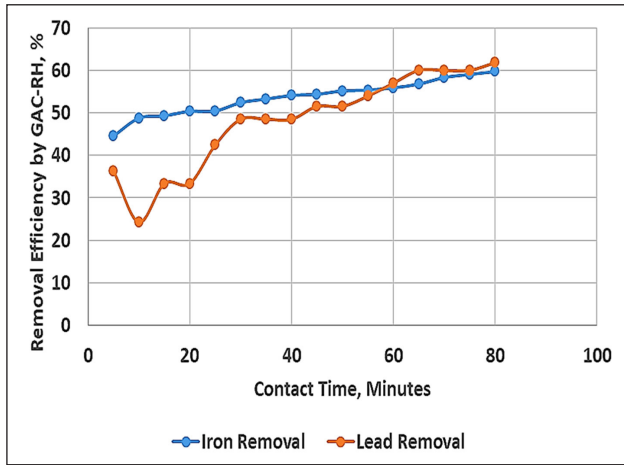
be attributed to intra-particle diffusion of the lead ions into the GAC–RH pores, as reported by Kumar et al. (2008).

It has been reported in the literature that optimum adsorbent dosage for metal removal generally ranges between 0.1 g and 3.5 g (Ho, 2008; Karthikeyan et al., 2007; Melese et al., 2020). Similarly, optimum contact times required for metal removal have varied between 30 min and 180 min (Melese et al., 2020; Malakootian et al., 2009; Desta, 2013).

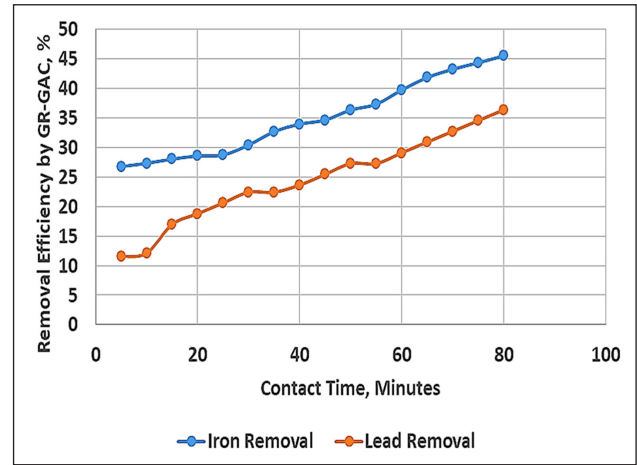
From the results obtained in this study, optimum dosage of 0.5 g each of GAC and RH resulted in maximum removal efficiencies of 60% and 62% (Fig. 14) for iron and lead, respectively, at equilibrium contact time of 80 min. Similarly, for the same optimum dosage of 0.5 g of GR and GAC, maximum removal efficiencies of 46% and 37% (Fig. 15) were achieved for iron and lead, respectively, at the same equilibrium contact time of 80 min.

#### Comparison of adsorption model performance for related research

Naiya et al. (2009) have reported the suitability of rice husk ash for the treatment of wastewater, with a 96.83% removal efficiency for lead using rice husk ash. This research also reported that the Freundlich isotherm model (with  $R^2 = 0.99$ ) performed better than the Langmuir isotherm model (with  $R^2 = 0.94$ ) in predicting the adsorption of lead onto rice husk ash. In the work carried out by Karnib et al. (2014), it was reported that the Freundlich isotherm model predicted the adsorption of lead from water onto activated carbon (with  $R^2 = 0.97$ ) better than the Langmuir isotherm model (with  $R^2 = 0.70$ ). Sizirici et al. (2017) reported that gravel can be used as adsorbent or filter to remove metals from polluted water.



**Figure 14.** Removal efficiency vs contact time for iron and lead using GAC-RH filter



**Figure 15.** Removal efficiency vs contact time for iron and lead using GR-GAC filter

**Table 4.** Comparison of adsorption modelling results of present study with other published work

Adsorbate	Adsorbent	Langmuir isotherm model	Freundlich isotherm model	Removal efficiency (%)	Reference
Iron	Maize cob	$R^2 = 0.977$ $R_L = 0.87$	$R^2 = 0.95$ $n = 3.9$	54	Nassar et al. (2004)
	Palm fruit bunch	$R^2 = 0.996$ $R_L = 0.86$	$R^2 = 0.99$ $n = 4.8$	79	
Lead	Commercially activated carbon	$R^2 = 0.997$ $R_L = 0.156$	$R^2 = 0.942$ $n = 2.88$	74	Jeyakumar and Chandrasekaran (2014)
	Sugarcane bagasse activated carbon	$R^2 = 0.95$ $R_L = 0.26$	$R^2 = 0.863$ $n = 1.92$	87	
Iron	Granular activated carbon – rice husk	$R^2 = 0.969$ $R_L = 0.358$	$R^2 = 0.916$ $n = 0.1296$	54	This research
	River gravel – granular activated carbon	$R^2 = 0.842$ $R_L = 0.466$	$R^2 = 0.645$ $n = 0.2007$	35	
Lead	Granular activated carbon – rice husk	$R^2 = 0.862$ $R_L = 0.518$	$R^2 = 0.634$ $n = 0.4675$	48	This research
	River gravel – granular activated carbon	$R^2 = 0.889$ $R_L = 0.518$	$R^2 = 0.814$ $n = 0.2378$	25	

From the adsorption modelling carried out, the Freundlich model predicted the adsorption of copper, iron and zinc from landfill leachate (with  $R^2$  of 0.94, 0.71, and 0.71, respectively) similar to the Langmuir model (with  $R^2$  of 0.97, 0.43 and 0.70, respectively). It is worthwhile to note that in this research, combined filter systems were developed, whereas the published works cited above were focused on singular filter materials.

Different researchers have reported on the effects of, inter alia, temperature, pH, concentration and contact time on adsorption. Senthil et al. (2010) reported that the rate of adsorption increases at lower concentration due to the fact that a larger surface area of the adsorbent is available for the process. Previous studies have also shown that adsorption capacity of the adsorbent increases with increasing pH of the adsorbent and decreases at lower pH (Ushakumary, 2013; Kaakani, 2012). Temperature gradient has been found to affect the solubility of the adsorbate, depending on the type of adsorbent used (Singh et al., 2021). It has been reported that an increase in temperature decreased the adsorption of copper ions and resulted in desorption from the surface of rice husk ash (Kashif et al., 2016). It has also been reported in the literature that the efficiency of the adsorbent in removing metal ions increases with increase in the dosage of adsorbent used (Jeyakumar and Chandrasekaran, 2014; Salihi et al., 2017). Previous publications have also reported that the uptake of metal ions increases with time until an optimum value is reached, after

which there is no more uptake of the metal ions (Mohammad et al., 2011; Azouaou et al., 2010; Martinez et al., 2006). At this optimum contact time, the maximum adsorption rate is attained (Ugwu et al., 2020).

Table 4 compares the model parameters and removal efficiencies obtained for the current study with other published work. This shows that even though the removal efficiencies of GAC-RH and GR-GAC were lower than for the other adsorbents in previous studies, GAC-RH performed well in the removal of iron and lead, with removal efficiencies of 54% and 48%, respectively. However, GR-GAC performed below average. This could be due to the fact that the surface area available for adsorption is not large enough to adsorb much of the adsorbate. Perhaps, chemical optimization of GAC-RH may enhance the removal efficiency of the adsorbent. It could also be observed that the Langmuir isotherm derived for this research showed a similar trend to that in the cited work in Table 4. However, the Freundlich isotherm derived for this research differed from the cited work as the  $n$  values obtained here showed that the nature of the adsorption processes predicted by the Freundlich isotherm model is chemisorption.

This study has reported  $R^2$  values of no less than 0.6, which showed a reasonable fit to the isotherm models. Further modification/optimization of the GAC-RH combined filter may improve adsorption capacity and removal efficiency of these combined adsorbents.



## CONCLUSIONS

The Langmuir and Freundlich isotherm models were applied to two low-cost combined filter systems, GAC–RH and GR–GAC, to predict the removal of iron and lead from automobile workshop stormwater runoff. The Langmuir model generally gave a better fit to measured data ( $R^2$  ranging from 0.842 to 0.963) when compared to the Freundlich model ( $R^2$  ranging from 0.634 to 0.916). The Langmuir isotherm model predicted the adsorption processes involved in this research as favourable, with  $R_L < 1$ . The Freundlich isotherm models predicted the adsorption processes as chemisorption with  $n < 1$ .

The adsorbent dosage and contact time influenced the adsorption capacity of the adsorbents used (granular activated carbon, rice husk and gravel) as well as the metal removal efficiencies of the filter systems. The study revealed that increased dosages of the GAC–RH and GR–GAC resulted in a decrease in the uptake of iron and lead, with optimum adsorbent dosage of 0.5 g. Also, the efficiencies of iron and lead removal by GAC–RH and GR–GAC increased with increase in the contact time, with optimum contact time of 80 min. Furthermore, it was found that the combined GAC–RH filter system produced higher removal efficiencies for iron and lead (54% and 48%, respectively) in comparison to the combined GR–GAC filter system (35% and 25%, respectively). The results have indicated that combined low-cost filters (GAC–RH and GR–GAC) can adsorb metals from polluted stormwater runoff from automobile workshops.

Further research towards modifying/optimizing the combined GAC–RH to increase its metal adsorption capacity and removal efficiency is warranted. Also, investigation of the performance of these models in the removal of oil and grease in automobile workshop stormwater using the same or modified/optimized combined filter systems is warranted.

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## CONFLICT OF INTEREST

The authors declare that there is no conflict of interest regarding the publication of this manuscript.

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