The use of compost as a sustainable solution to treat contaminated wastewater

Sinmi Abosede

Abstract — This study evaluates the feasibility of two types of commercially available compost materials, Household Compost (HC) and African Violet Compost (AC) to treat contaminated wastewater effluents, containing phenol. The compost materials were used in their unrefined state without any pretreatment, making them an attractive sustainable resource. The impact of various experimental conditions such as initial pH, contact time and temperature on the removal of phenol by the compost materials, was determined by batch tests. The adsorption kinetics were analysed using the pseudo-first order, pseudo-second order, Elovich and intraparticle diffusion models, while the equilibrium isotherms were analysed with the Freundlich, Langmuir and Redlich-Peterson isotherm models. Kinetic and isotherm parameters were calculated through the use of non-linear regression and error analysis and used to determine the optimum models. Adsorption kinetics for the rate of adsorption of phenol on the AC compost followed the Elovich kinetic model, while the pseudo first order model adequately described the rate of adsorption of phenol on the HC compost. AC and HC compost had a maximum capacity of 2.29 mg/g and 1.52 mg/g respectively. The Freundlich isotherm best described the adsorption of phenol by AC compost, while the Langmuir and Redlich-Peterson isotherms best described, the adsorption of phenol on HC compost. Thermodynamics studies showed that the removal of phenol on the compost was an endothermic process.

Index Terms — Adsorption, Compost, Low cost materials, Organic Pollutants, Sustainability, Phenol, Wastewater treatment

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1 INTRODUCTION

Phenolic compounds are commonly found in industrial effluents generated from petroleum refineries, coke plants and plastic and resin industries. The United States Environmental Protection Agency (USEPA) and the European Union (EU) have listed phenolic compounds as priority pollutants. They are toxic and carcinogenic compounds and their presence in natural waters and drinking water is detrimental to humans and animals at low concentrations [1], as they have adverse effects on the internal and external organs of humans and animals [2]. As a result, the treatment of wastewater containing phenolic compounds is critical to protect human and animal life.

Typical processes used in the removal of phenol from wastewater, include biological treatment, ion-exchange, disinfection, chemical precipitation, coagulation and flocculation, reverse osmosis and adsorption [3]–[9]. The most common process is adsorption and adsorption by activated carbon has been used extensively to remove phenol from wastewater. Activated carbon is a popular choice for a suitable absorbent because of its high adsorption capacity for a variety of organic pollutants. However, it is often not a viable economic solution because of its high initial cost and expensive regeneration process.

As result, the use of low cost adsorbents in the removal of toxic pollutants from wastewater effluent has gained widespread acceptance in recent years, as they offer potentially simple, sustainable and economic solutions to the challenges imposed by the presence of toxic pollutants in the environment. An adsorbent can be considered low cost, if it requires minimal pre-treatment and can be found in large quantities in nature [10].

Several low cost adsorbents have been used for the treatment of wastewater contaminated with phenol. These have included the use of rice husk, [11]; sludge [1]; red mud [12]; industrial waste [13]; chitosan [14] and eggshell [15]. Most of the previous work in this area, has focused on the use of use of various pretreatment processes to increase the adsorption capacity of the adsorbents. This leads to an increase in cost and problems linked with the disposal of the adsorbent [16].

This study has focused on the use of a simple and sustainable technology, using compost, a low cost material in its natural state, without any pretreatment, to remove phenol from wastewater effluent. Compost has been successfully used to remove various contaminants from contaminated effluents, these include pesticides [17]; colorants [18] and heavy metals [19]. The proposed process involves contacting the compost with the contaminated effluent for a period of time. This is followed by the separation of the spent compost and phenol by separation processes such as centrifugation, filtration and flocculation.

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2 MATERIALS AND METHODS

2.1 Adsorbent preparation and characterisation

Compost samples called Household compost (HC) and African-violet compost (AC) were obtained from a household retailer. The Household compost (HC) is a peat-based compost

extracted from natural wildlife sites, consisting of sphagnum moss peat and dolomitic lime. The African-violet compost is a man-made compost from the decomposition of natural recycled products. The compost samples were air-dried and sieved with a 500 µm sieve before use. Various characterization tests were carried out on the two compost samples, to determine the properties that make them suitable sorbents. These included the determination of the organic matter, organic carbon, moisture content; surface area analysis, pH and electrical conductivity.

2.2 Adsorbate

Phenol (99% pure) was supplied by Aldrich Chemicals. 1g of phenol was dissolved in 1000ml of distilled water, to make a stock solution with a concentration of 1000mg/l. Various solutions of phenol containing different concentrations were obtained by diluting the stock solution. The concentrations of phenol in solution were determined by a High Performance Liquid Chromatography (HPLC) system, which utilized an UV detector set at a wavelength of 280 nm, with a Supelcosil LC-8 column supplied by SUPELCO.

2.3 Batch experiments

Adsorption isotherms were determined using the batch technique. 1 g of compost was weighed and added to 250 ml pyrex glass conical flasks, containing 100 ml phenol solutions at various concentrations ranging from 10 - 90 mg/l. The samples were shaken on a mechanical shaker at room temperature of 21°C, until equilibrium was attained (about 6 hours). After equilibration, the solid phase was removed by a centrifugation step, to separate the solid particles from solution and a flocculation step using Ferric Chloride, to remove the colloidal particles from the solution. After filtration through a 0.45 µm filter, the samples were analysed for residual phenol using the HPLC system

The amount of phenol adsorbed, qe (mg/g) by the compost samples was determined as follows:

$$q_e = \frac{c_o - c_e}{W} \qquad (1)$$

where Co is the initial concentration of the phenol in solution, Ce is the equilibrium concentration of the phenol in aqueous solution (mg/L) and W is the dose of the compost (g/L).

Using a similar procedure, a time-dependence study was conducted to study the kinetics of the uptake of phenol by the HC and the AC compost samples and to determine the time taken for equilibrium to be attained. At a set initial concentration of 50 mg/l, various samples containing different concentrations of phenol, were contacted with the compost samples and shaken on a mechanical shaker. At periodic intervals ranging from 30 mins - 24 hours, each flask was removed, separat-

ed and analysed for phenol. The amount of phenol adsorbed at the different time intervals, time t, was calculated as follows:

$$q_t = \frac{(C_0 - C_t)}{W} \qquad (2)$$

where q_t (mg/g) and C_t (mg/l) represent the amount of phenol adsorbed at time t and the aqueous concentration of phenol at time t, respectively.

The effect of pH on the removal of phenol by the HC compost was investigated, by varying the pH of the solution from 3 to 10, using 0.5M Sodium Hydroxide and 0.1M Hydrochloric acid solutions. 1g of the compost was added to the different pH solutions, containing 100 ml portions of solution containing phenol with a concentration of 40 mg/l. The samples were shaken for 10 hours, separated and analysed for phenol.

The effect of temperature on the removal of phenol by the HC compost was investigated at 5°C, 21°C and 30°C. A water bath was used to regulate temperature and the experiments were conducted at pH3 to minimise the dissolution of colloidal particles from the compost. The samples were shaken for 10 hours, separated and analysed for phenol.

Blank experiments without the compost were conducted to determine if the glass containers and the flocculation step contributed to the removal of phenol from solution and it was discovered that they did not contribute to the removal of phenol. All adsorption experiments were performed in duplicate and the average values were used.

3 RESULTS AND DISCUSSION

3.1 Characterisation of adsorbents

The physio-chemical characteristics of the AC and HC compost are presented in Table 1. The two compost samples have similar characteristics, expect for their organic matter content. The organic matter content of the HC compost is 92.50%, while that of the AC compost is 54.72%. This difference can be attributed to the fact that the AC compost is made from man-made natural recycled products and is likely to contain more inorganic material than HC compost which is peat based. Peat is predominantly made of organic compounds such as lignin, and humic substances [20].

Table 1
Properties of HC and AV compost samples

Parameter	HC compost	AC Compost
Organic matter (%)	92.50	54.72
Moisture content (%)	15.50	10.10
Dissolved organic carbon (mg/l)	17.42	12.30
Organic carbon (g OC/l)	4.6	2.70
UV absorbance at 254 nm	0.51	0.72
Surface area (m^2/g)	0.90	0.32
pH	7.25	7.58
Conductivity (mS)	0.723	0.761

Fig. 1. Effect of pH on the removal of phenol by HC compost, initial phenol concentration = 40 mg/l, equilibration time = 10 hours

3.3 Effect of temperature on the removal of phenol

The removal of phenol by the HC compost was carried out at temperatures of 5oC, 21oC and 30oC (273K, 298K and 303K). The percentage removal of phenol is plotted as a function of temperature in Fig. 2. The plot shows that that the percentage removal of phenol increases with increasing temperature. This is consistent with results obtained by Srivastava et al. 2006 [23] for the removal of phenol by fly ash. The increase in the removal of phenol with increasing temperature can be attributed to chemisorption, due to an increase in the formation of chemical bonds between the surface of the compost and the phenol molecule.

3.2 Effect of pH on the removal of phenol

Fig. 1 shows that amount of phenol removed from solution decreases with increasing pH. The pH of the solution has a significant impact on the removal of phenol. Phenol is a weak acid with a pK$_a$ of 9.98 and at lower pH values, it exists in its molecular state. At pH values higher than the pK$_a$, it exists in its ionised, negatively charged state. This ionised state is more soluble than the molecular state and has a lesser tendency to be adsorbed by the compost. In addition, the negative charges on the surface of the compost will increase with pH and this will lead to electrostatic repulsion with the ionised phenol. A similar observation was made by Kumar et al. 2010 [21] and Soni et al. 2017 [22] in their studies on the removal of phenol by chitosan and by Srivastava et al. 2006 [23] in their studies on the removal of phenol by fly ash. The optimum pH for maximum removal was pH 3, however to maintain the low cost strategy of the project and avoid the addition of acid for pH corretion, the experiments were carried out at the natural pH of the compost samples in solution, which was between 7.25 and 7.58.
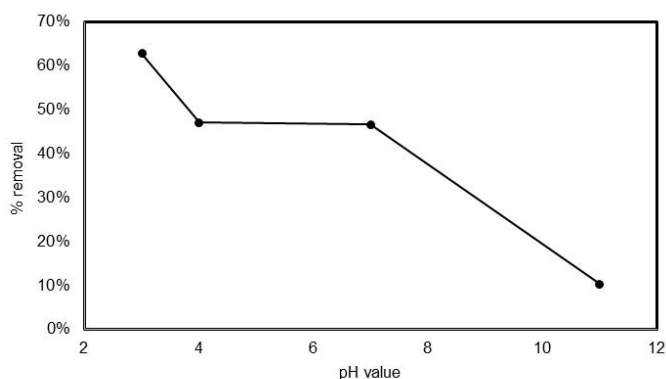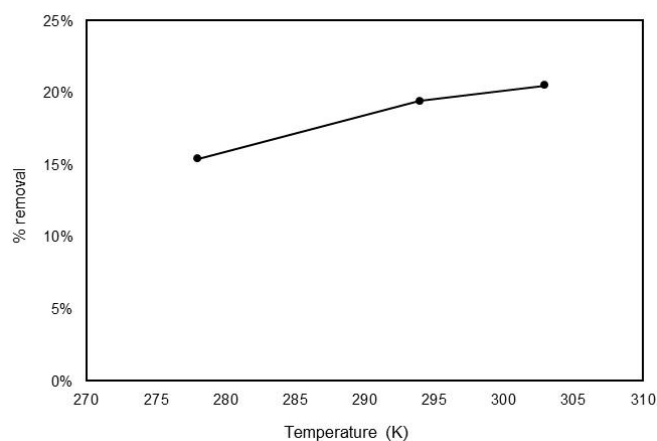

Fig. 2. Effect of temperature on the removal of phenol by HC compost (pH = 2, initial concentration of phenol = 74 mg/l, compost dose = 1g/100 ml)

3.4 Thermodynamic Study

The mechanism of adsorption may be determined by calculating thermodynamic parameters such as change in Gibbs free energy (ΔG), change in enthalpy of adsorption (ΔH), and change in entropy (ΔS). This can be calculated as follows [24]:

$$\Delta G = -RT\ln K \qquad (3)$$

$$\Delta G = \Delta H - T\Delta S \qquad (4)$$

$$\ln K = \frac{\Delta H}{RT} + \frac{\Delta S}{R} \qquad (5)$$

$$K_c = \frac{q_e}{C_e} \qquad (6)$$

where K_c is the equilibrium constant, q_e and C_e are the equilibrium concentrations (mg/l) of phenol on the adsorbent and in the solution respectively, T is the temperature (Kelvin) and R is the universal gas constant (8.314 J/mol K). Using Equation 5, the Van't Hoff plot (Fig. 3) was obtained by plotting $\ln K_c$ against (1/T) and ΔH and ΔS were calculated from the slope and intercept. Table 2 gives the thermodynamic parameters of the adsorption of phenol onto the HC compost. The standard Gibbs free energies (ΔG) at the temperatures studied were negative, this indicates that the adsorption of phenol on HC compost was feasible and spontaneous [25]. The change in adsorption standard enthalpy was a positive value at 10.01 kJ/mol, indicating that the adsorption of phenol on the HC compost is endothermic [23], while the positive value of change in standard entropy (ΔS) suggests an increased randomness at the solid/solution interface during the adsorption [20].
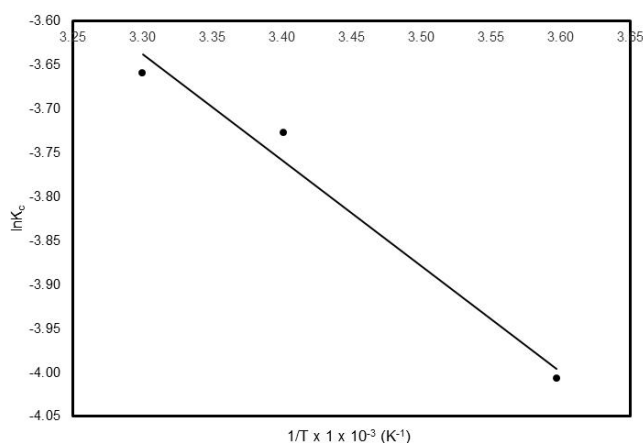

Fig.3. Van't Hoff plot for the adsorption of phenol onto HC compost

Table 2
Thermodynamic parameters for the adsorption of phenol onto HC compost

Temperature (K)	Δ H (kJ/mol)	Δ S (kJ/mol. K)	Δ G (kJ/mol)
278	10.01	2.80	-768.66
294			-813.48
303			-838.68

3.5 Effect of contact time on the removal of phenol

The effect of contact time on the removal of phenol by the HC and AC compost was studied and is presented is Fig. 4. The results, show that equilibrium was attained in about 6 hours for the two compost samples.
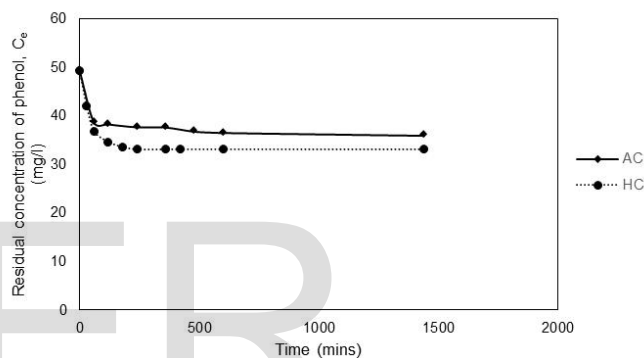

Fig.4.   Effect of contact time on the adsorption of phenol on HC and AC compost. pH= 7.25 – 7.58; initial concentration of phenol = 50 mg/l, Temperature = 21°C; Compost dose = 10 g/L

3.6 Adsorption kinetics

It is important to study the kinetics in order to be able to design appropriate adsorption treatment systems. It provides a better understanding of the reaction pathway and the mechanism of adsorption. Kinetic models are used to determine the mechanism and rate controlling step.

It is well documented that the adsorption of an adsorbate from the liquid phase on an adsorbent usually involves four main steps; (i) transport of the adsorbent in the bulk aqueous solution (ii) film diffusion, (iii) intraparticle diffusion in the pores and (iv) surface reaction on active surface sites on the adsorbent [23], [26]. Steps (i), (ii) and (iii) are transport mechanisms, while surface reaction is a chemical reaction step. The overall rate of adsorption is controlled by the slowest of all the four steps and this can be any of the steps or in some cases by a combination of all the steps [27]. However, in a fully mixed batch reactor, step (i) is usually very fast and is usually neglected.

Researchers [28]–[30] have shown that the intraparticle diffusion model is applicable, when the controlling step is the transfer of adsorbate to surface sites on the adsorbent (step ii), whereas the pseudo - first order, pseudo-second order and Elovich kinetic models are applicable when the chemical surface reaction is the controlling step (step iii). In this study, the applicability of the pseudo first order, pseudo second order, the Elovich kinetic models and the intra-particle diffusion model were examined at a constant temperature of 21°C for the removal of phenol by the HC and AC compost.

The pseudo first-order model [31] is generally expressed as follows:

$$\frac{dq_t}{dt} = k_1\left(q_e\text{-}q_t\right) \tag{7}$$

where q_e (mg/g) and q_t (mg/g) are the adsorption capacity at equilibrium and at time t, respectively, and k_1 (1/min) is the rate constant of pseudo first-order. Integrating (7), applying initial conditions of t = 0 and q_t = 0 and rearranging gives the following relationship between q_t and t:

$$q_t = q_e\left[1\text{-}\exp\left(\text{-}k_1 t\right)\right] \tag{8}$$

The Pseudo-second order model [32] is expressed as follows:

$$\frac{dq_t}{dt} = k_2(q_e\text{-} q_t)^2 \tag{9}$$

where q_e and q_t are the adsorption capacity at equilibrium and at time t, respectively and k_2 is the rate constant of pseudo-second order adsorption (g/(mg min)).

Integrating (9) and applying the initial conditions of t = 0 and q_t = 0 and rearranging gives the following equation between q_t and t:

$$q_t = \frac{k_2 q_e^2 t}{1+k_2 q_e t} \tag{10}$$

The Elovich model [33] is expressed as follows:

$$\frac{dq_t}{dt} = \alpha\exp(\text{-}\beta q_t) \tag{11}$$

where q_t is the sorption capacity at time t (mg/g), α is the initial sorption rate (mg/g/min) and β is the desorption constant (g/mg).

Equation 11 can be simplified by assuming $\alpha\beta t \gg 1$, integrating and applying the initial conditions of t = 0 and q_t = 0, to give:

$$q_t = \frac{1}{\beta}(\ln\alpha\beta) + \frac{1}{\beta}\ln t \tag{12}$$

The intra-particle diffusion model [34] is expressed as follows:

$$q_t = k_p\sqrt{t} + C \tag{13}$$

where k_p (mg/(g min)$^{1/2}$) is the intraparticle diffusion rate constant and C is a constant related to the boundary layer effect. The plot of q_t vs $\sqrt{t}$ should be linear if intraparticle diffusion is involved in the adsorption process and if the plot passes through the origin, then intraparticle diffusion should be the rate-controlling step.

The experimental data for the uptake of phenol, q_t versus time was fitted to the pseudo-first order, pseudo-second order and Elovich kinetic models by non-linear regression using Microsoft Excel Solver. To quantitatively compare the fitness of the models, error functions (Table 4) such as coefficient of determination (r^2), Average relative errors (ARE) and Hybrid fractional error (HYBRID) were determined for each kinetic model. The results are shown in Figs. 5 and 6 and the kinetic parameters and the error functions were determined and are presented in Table 3.
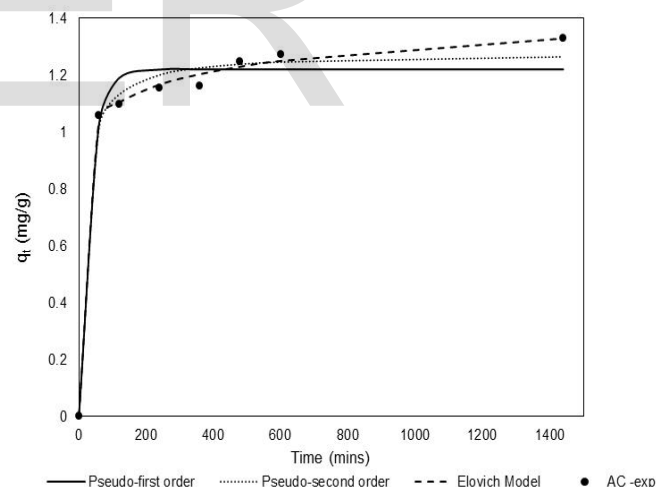

Fig.5. The fitting of the adsorption data for the adsorption of phenol on AC compost to various kinetic models pH = 7.58; initial concentration of phenol = 50 mg/l, Temperature = 21°C; Compost dose = 10 g/L
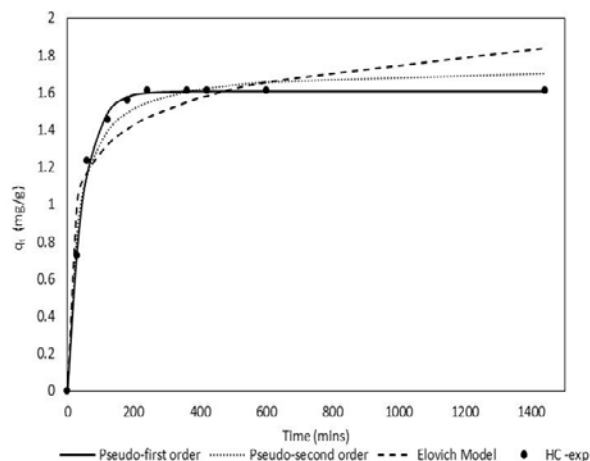
Fig.6. The fitting of the adsorption data for the adsorption of phenol on HC compost to various kinetic models pH= 7.25; initial concentration of phenol = 50 mg/l, Temperature = 21°C; Compost dose = 10 g/L

Table 3
Kinetic parameters for the adsorption of phenol to AC and HC compost

Kinetic Model	Parameter	AC Compost	HC Compost
Pseudo-first order	k_1 (min^{-1})	0.03	0.02
	$q_{e, mea}$ (mg/g)	1.33	1.61
	$q_{e,calc}$ (mg/g)	1.22	1.61
	r^2	0.64	0.99
	HYBRID	0.55	0.10
	ARE	3.44	1.75
Pseudo-second order	k_2 (g/ mg min)	0.05	0.02
	$q_{e, mea}$ (mg/g)	1.33	1.61
	$q_{e, calc}$ (mg/g)	1.28	1.74
	r^2	0.80	0.93
	HYBRID	0.24	0.20
	ARE	3.49	2.51
Elovich Model	α (mg/ (g min))	147.62	0.96
	β (g/mg)	11.03	4.79
	r^2	0.95	0.76
	HYBRID	0.05	0.69
	ARE	0.95	4.59
Intraparticle Diffusion	k_p (mg/g min$^{0.5}$)	0.01	
	r^2	0.92	N/A
	HYBRID	0.05	
	ARE	1.27	

Fig.5 and Table 3, indicates that the Elovich kinetic model is more suitable for describing the rate of adsorption of phenol on the AC compost, than the pseudo-first order and pseudo-second order kinetic models. This model provides the best fit of experimental data to the kinetic model for the removal of phenol by the AC compost. This is further verified by the relatively high value of the correlation coefficient r^2 value and lowest error values for the Elovich model, in comparison to the other two kinetic models. Adsorption of phenol on soil has been successfully described by the Elovich model [16]. In the Elovich model, the rate of adsorption is closely related to the change in the adsorption capacity of the adsorbent surface [26]. This suggests that the chemical interaction between the phenol and the active sites on the surface of the AC compost is one of the mechanisms involved in the removal of phenol by AC compost.

From Fig.6 and Table 3, it can be seen that pseudo-first order kinetic model is more suitable for describing the rate of adsorption of phenol on the HC compost, in comparison to the pseudo-second order and Elovich model. This model provides the best fit of experimental data to the kinetic model for the adsorption of the phenol on the HC compost. This is further verified by the relatively high value of the correlation coefficient r^2 value and lowest error values for the pseudo-first order, in comparison to the other two kinetic models. This is indicative of a chemisorption mechanism and similar observations was made for the adsorption of phenol on activated carbon [35] and the adsorption of phenol by water hyacinth [36], who found that the adsorption of phenol on these materials could be described by the pseudo-first order reaction.

From Fig. 7 it can be seen that the intraparticle diffusion is one of the mechanisms involved in the removal of phenol by the AC compost, as the plot of plot of q_t vs $\sqrt{t}$ can be represented by a linear equation. However, the plot does not pass through the origin, so this indicates that while intraparticle diffusion was involved in the adsorption process, it is not the only rate controlling step and some other kinetic mechanisms were controlling the rate of adsorption [37],[38]. Fig.7 shows that intraparticle diffusion is not involved in the removal of phenol by the HC compost, as the plot of q_t vs $\sqrt{t}$ is not a linear plot.
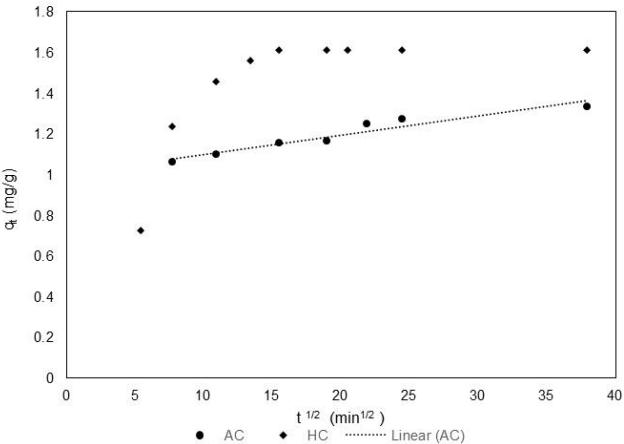

Fig.7. Intraparticle plot for the adsorption of phenol on AC and HC compost pH= 7.25 – 7.58; initial concentration of phenol = 50 mg/l, Temperature = 21°C; Compost dose = 10 g/L

3.7 Adsorption Isotherm

In order to assess the suitability of a potential adsorbent, it is essential to determine the most appropriate adsorption isotherm. Adsorption isotherms are used to describe the equilibrium relationship between an adsorbate and adsorbent in an adsorption system. They are mathematical equations expressing the relationship between the amount adsorbed by the adsorbent and the amount of adsorbate remaining in solution at a fixed temperature. They are an important tool used to optimize the design of an adsorption system to remove pollutants from wastewater. The adsorption parameters give an insight into the adsorption mechanism, the surface characteristics of the adsorbent and the affinity of a particular adsorbent for an adsorbate. The adsorption behavior of phenol on the two types of compost was investigated by using the Langmuir, Freundlich and the Redlich- Peterson isotherms.

The Freundlich model [39] is commonly used to describe sorption on heterogeneous surfaces. It is an empirical model and is based on the assumption that there are multiple adsorption sites on the adsorbent acting in parallel with each exhibiting a different adsorption free energy.

It is described by the equation:

$$q_e = K_f C_e^{1/n} \qquad (14)$$

where K_f (mg/g) is the measure of the adsorption capacity and $1/n$ is a measure of the adsorption intensity or surface heterogeneity, with heterogeneity increasing as its value approaches zero. If $1/n$ is less than 1, this indicates a chemisorption process, while a value greater than one is indicative of a physical adsorption process [40]. One of the limitations of Freundlich isotherm is that is does not follow Henry's Law at low concentrations and does not converge to a linear isotherm at low concentrations of C_e, making it thermodynamically inconsistent.

The Langmuir model [41] is an empirical model that is based on the assumption that adsorption takes place on a fixed number of homogenous sites on the surface of the absorbent, that are energetically uniform and that there are no interactions between neighbouring adsorbed molecules. It is usually expressed by an equation of the form:

$$q_e = \frac{Q_L b C_e}{1 + b C_e} \qquad (15)$$

where Q_L (mg/g) is a measure of the adsorption capacity of the adsorbent and b (L/mg) is a measure of the adsorption energy.

The Redlich-Peterson model [42] is a hybrid isotherm that features elements of both the Freundlich and Langmuir isotherms. It can be used to describe adsorption equilibria over a wide concentration range and can be applied to either homogenous or heterogeneous surfaces. It is expressed by the following equation:

$$q_e = \frac{K_R C_e}{1 + a_R C_e^g} \qquad (16)$$

where K_R (L/mg) and a_R (L/mg) are isotherm constants and g is an exponent. By comparing equations 15 and 16, it can be seen that the Redlich-Peterson isotherm will represent the Langmuir isotherm, when g = 1.

Nonlinear regression analysis was performed to determine the values of the isotherm model parameter, using an optimisation procedure with the solver add-in function of Microsoft Excel. The optimisation procedure involved the use of the generalised reduced gradient algorithm (GRG) in solver, to determine the isotherm parameters by using error functions as objective functions to minimise or maximize the error distribution between the isotherm equation and experimental data. The error functions (Table 4) utilised include the coefficient of determination (r^2), Sum of the square of errors (ERRSQ), Hybrid fractional error function (HYBRID), Average relative error (ARE), and Sum of the absolute errors (EABS). he use of these error functions to determine isotherm parameters is consistent with work by other researchers [23], [43]–[45]. Each of the error functions produced a different set of isotherm parameters and a normalisation procedure was employed to provide a comparison of the different parameter sets and to determine the optimum parameter set [46], [47]. This normalisation involved the determination of a sum of normalised errors (SNE) for each parameter set for each isotherm. This was determined as follows:

1. Select an error function and determine the isotherm parameter set that minimises or maximises (in the case of r^2) the error function;
2. Determine the values of the other error functions based on the isotherm parameters from (i);
3. Perform the same procedure listed in (i) and (ii) for the other error sets
4. Calculate the normalised error, by the dividing the error value for each function by the maximum error value
5. Sum the normalised errors for each parameter set, to give the sum of normalised errors (SNE).

The optimum isotherm model for a particular error function is the parameter set that provides the smallest normalised error (SNE).

The values of the parameters for the Langmuir, Freundlich and Redlich-Peterson isotherms and the corresponding error values are presented in Tables 5 and 6. The lowest values of the SNE for each isotherm parameter set are indicated in the table in bold. For the adsorption of phenol on the AC compost,

the ERRSQ error function had the lowest SNE value and provided the best fit for the Langmuir and Redlich-Peterson isotherms, while the ARE error function had the lowest SNE value and provided the best fit for the Freundlich isotherm. For the adsorption of phenol on the HC compost, the ERRSQ error function had the lowest SNE value for the Freundlich and Redlich-Peterson isotherm, while the Chi-test had the lowest SNE value and the best fit for the Langmuir isotherm.

The values of the parameters for the Langmuir, Freundlich and Redlich-Peterson isotherms and the corresponding error values are presented in Appendix 1. The lowest values of the SNE for each isotherm parameter set are indicated in the table in bold. For the adsorption of phenol on the AC compost, the ERRSQ error function had the lowest SNE value and provided the best fit for the Langmuir and Redlich-Peterson isotherms, while the ARE error function had the lowest SNE value and provided the best fit for the Freundlich isotherm. For the adsorption of phenol on the HC compost, the ERRSQ error function had the lowest SNE value for the Freundlich and Redlich-Peterson isotherm, while the Chi-test had the lowest SNE value and the best fit for the Langmuir isotherm.

Table 4
List of error functions

Error Function	Mathematical expression
Coefficient of determination (R^2)	$$\frac{\sum_{i=1}^{n}(q_{e\,cal} - \overline{q_{e\,meas}})^2}{\sum_{i=1}^{n}(q_{e\,cal} - \overline{q_{e\,meas}})^2 + (q_{e\,cal} - q_{e\,meas})^2}$$
Sum of the absolute errors (EABS)	$$\sum_{i=1}^{n} |q_{e\,meas} - q_{e\,cal}|$$
Sum of the squares of errors (ERRSQ)	$$\sum_{i=1}^{n} (q_{e\,cal} - q_{e\,meas})^2$$
Average relative error (ARE)	$$\frac{100}{p} \sum_{i=1}^{n} \left| \frac{(q_{e\,cal} - q_{e\,meas})}{q_{e\,cal}} \right|$$
Hybrid fractional error function (HYBRID)	$$\frac{100}{n-p} \sum_{i=1}^{n} \left[\frac{(q_{e\,cal} - q_{e\,meas})^2}{q_{e\,cal}} \right]$$
Chi-test	$$\sum_{i=1}^{n} \left[\frac{(q_{e\,cal} - q_{e\,meas})^2}{q_{e\,cal}} \right]$$

$q_{e\,meas}$ experimental measurement of the concentration of phenol adsorbed; $q_{e\,cal}$ - calculated value of adsorbed using isotherm model; n - the number of experimental data points; p - the number of parameters in each isotherm model.

The ERRSQ error functions provided the best overall results for the isotherms studied. Table 5 summarizes the isotherms parameters providing the best fit to experimental based on the ERRSQ error values. Fig.8 and Fig. 9 shows the comparison of the experimental equilibrium data with the calculated values from the optimum isotherm parameters obtained for the adsorption of phenol on AC and HC compost respectively. For the adsorption of phenol on the AC compost, the Freundlich isotherm has the lowest ERRSQ value and thus provides the best fit in comparison to the equilibrium data, while for the adsorption of phenol on the HC compost, the Langmuir and Redlich-Peterson isotherms have the lowest ERRSQ value, thus providing the best fit in comparison to equilibrium data. The Redlich-Peterson and Langmuir isotherm overlap, because the Redlich-Peterson constant g is 0.99 and thus approximates to the Langmuir isotherm.

The removal of phenol by other low-cost adsorbents such as dried activated sludge, peat and chitosan has been successfully described by the Langmuir isotherm, Freundlich and the Redlich-Peterson isotherms [22], [48], [49]. The maximum adsorption capacity of the AC and HC compost for phenol was determined to be 2.29mg/g and 1.52 mg/g respectively. The maximum percentage removal for both types of compost ranged from 45% - 48%. Table 6 presents the adsorption capacities of various adsorbents for phenol. Each adsorbent has its specific physio-chemical properties and the experimental conditions for adsorption will vary across the different studies. However, it can be seen that the performance of the AC and HC compost materials for the removal of phenol is comparable to other low-cost materials such as rice husk and aged-refuse. In this study, compost was used in its unrefined state without any pretreatment. It is likely that the adsorption capacity of the compost will increase with chemical pretreatment processes, as this will most likely increase the active sites on the surface of compost. However, this will not be cost-effective on a large scale and will deviate from the low-cost strategy of the study.
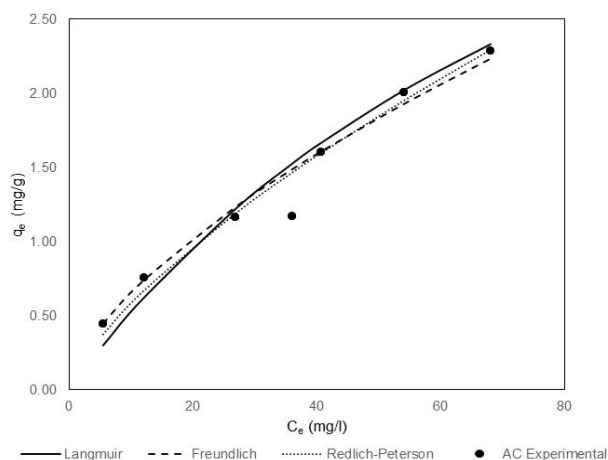

Fig. 8. Equilibrium isotherms for the adsorption of phenol of AC compost
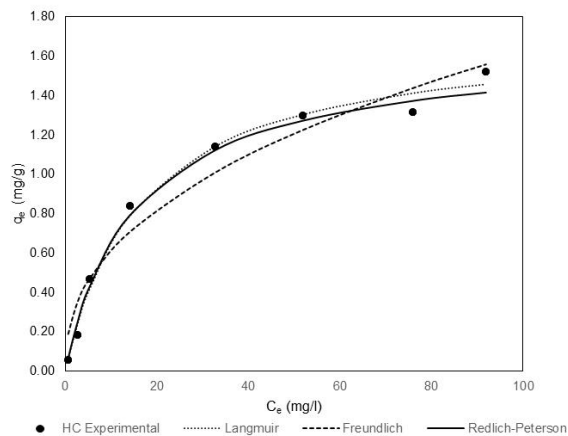
Fig. 9. Equilibrium isotherms for the adsorption of phenol of HC compost

Table 5
Best fit model for the different adsorption isotherms based on ERRSQ error function

Compost	Isotherm	Parameters
	Langmuir	
	Q (mg/g)	5.76
	b (L/mg)	0.01
	ERRSQ	0.14
	Freundlich	
	K (mg/g)	0.11
AC	1/n	0.71
	ERRSQ	0.09
	Redlich-Peterson	
	K (L/g)	0.28
	a (L/mg)	1.74
	g	0.34
	ERRSQ	0.10
	Langmuir	
	Q (mg/g)	1.68
	b (L/mg)	0.07
	ERRSQ	0.02
	Freundlich	
	K (mg/g)	0.23
HC	1/n	0.42
	ERRSQ	0.10
	Redlich-Peterson	
	K (L/g)	0.11
	a (L/mg)	0.07
	g	0.99
	ERRSQ	0.02

Table 6
Comparison of phenol adsorption on various low-cost adsorbents

Adsorbent	Capacity (mg/g)	References
Sewage Sludge	94	[50]
Activated sludge	86.1	[51]
Activated Carbon	13.22	[52]
Rice husk	4.508	[53]
Fungal Biomass	13.48	[54]
Aged-refuse	0.597	[55]
Luffa Cylindrica fibers	10.37	[25]
Zeolitic Composite	0.53	[56]
AC Compost	2.29	This Study
HC Compost	1.52	This Study

4 CONCLUSION

The potential of two types of compost - AC and HC compost to remove phenol from wastewater was investigated. The adsorption of phenol on the compost was found to be dependent on pH and temperature. The optimum pH for adsorption was pH3, however most of the experiments were conducted at the natural pH (~7) of the adsorption systems, in order to maintain the low cost strategy of the study. The adsorption of phenol on the HC compost increased with temperature, indicating an endothermic process, with a positive ΔH of 10.01 kJ/mol.

Equilibrium was attained in about 6 hours for both types of compost. The Elovich kinetic model provided the best fit for the rate of adsorption of phenol on the AC compost and the results showed that intraparticle diffusion was involved in theadsorption process. The pseudo first order model, provided the best for the rate of adsorption of phenol on the HC compost and intraparticle diffusion was not involved in the adsorption process.

Equilibrium adsorption isotherms for the adsorption of phenol on the AC and HC compost were determined at pH7, temperature of 21ºC and compost dose of 10g/l. The equilibrium data describing the adsorption of phenol on the AC compost was best described by the Freundlich isotherm, indicating that the surface of the compost is heterogeneous in nature. The equilibrium adsorption data for the adsorption of phenol on the HC compost was best described by the Langmuir and Redlich-Peterson isotherms, indicating monolayer adsorption on a homogenous surface, with saturation of active sites on the surface of the compost, as the concentration of phenol in solution increases.

This study showed that compost was an efficient low cost adsorbent that could successfully be used in a sustainable manner to remove phenol from contaminated wastewater effluent..

5 APPENDIX A

Isotherm parameters and error values for the adsorption of phenol on AC compost (Values in bold represent minimum sum of normalized errors (SNE))

	r²	Chi test	ERRSQ	HYBRID	ARE	EABS
Langmuir						
Q_L (mg/g)	5.78	3.98	5.76	3.98	3.04	6.14
b (L/mg)	0.01	0.02	0.01	0.02	0.03	0.01
R²	0.95	0.94	0.95	0.94	0.91	0.95
Chi test	0.17	0.15	0.17	0.15	0.18	0.17
ERRSQ	0.14	0.17	0.14	0.17	0.26	0.15
HYBRID	3.40	2.99	3.39	2.99	3.51	3.50
ARE	12.95	12.11	12.87	12.11	10.44	12.43
EABS	0.75	0.90	0.75	0.90	1.01	0.67
SNE	5.94	5.63	**3.94**	5.63	5.63	4.94
Freundlich						
K_f (mg/g)	0.11	0.13	0.11	0.13	0.15	0.13
1/n	0.71	0.66	0.71	0.66	0.64	0.68
r²	0.97	0.96	0.97	0.96	0.96	0.96
Chi test	0.09	0.08	0.09	0.08	0.09	0.09
ERRSQ	0.09	0.10	0.09	0.10	0.11	0.11
HYBRID	1.73	1.59	1.73	1.59	1.83	1.82
ARE	8.40	7.56	8.39	7.56	7.56	6.81
EABS	0.59	0.65	0.59	0.65	0.65	0.50
SNE	5.98	5.61	5.44	5.61	**5.31**	5.40
Redlich - Peterson						
K_R (l/g)	2.43	0.60	0.28	0.37	0.41	0.58
a_R (l/mg)	20.70	3.79	1.74	2.11	1.98	3.93
g	0.30	0.37	0.34	0.38	0.42	0.34
r²	0.97	0.96	0.96	0.96	0.96	0.96
Chi test	0.09	0.08	0.09	0.08	0.10	0.09
ERRSQ	0.09	0.10	0.10	0.10	0.12	0.10
HYBRID	2.16	2.04	2.30	2.08	2.44	2.30
ARE	8.43	7.78	8.86	7.83	6.15	7.31
EABS	0.59	0.66	0.60	0.65	0.57	0.51
SNE	5.98	5.49	**5.15**	5.46	5.23	5.44

Isotherm parameters and error values for the adsorption of phenol on HC compost (Values in bold represent minimum sum of normalized errors (SNE))

	r²	Chi test	ERRSQ	HYBRID	ARE	EABS
Langmuir						
Q_L (mg/g)	1.68	1.72	1.68	1.72	1.82	1.64
b (L/mg)	0.07	0.06	0.07	0.06	0.05	0.07
r²	0.99	0.99	0.99	0.99	0.99	0.99
Chi test	0.04	0.03	0.04	0.03	0.04	0.05
ERRSQ	0.02	0.02	0.02	0.02	0.03	0.02
HYBRID	0.60	0.53	0.60	0.53	0.63	0.86
ARE	9.19	7.95	9.19	7.95	6.95	10.74
EABS	0.30	0.33	0.30	0.33	0.36	0.29
SNE	5.99	**4.27**	4.37	4.37	4.84	5.34
Freundlich						
K_f (mg/g)	0.23	0.14	0.23	0.14	0.10	0.14
1/n	0.42	0.55	0.42	0.55	0.64	0.55
R²	0.96	0.93	0.96	0.93	0.87	0.92
Chi test	0.52	0.24	0.52	0.24	0.33	0.27
ERRSQ	0.10	0.17	0.10	0.17	0.32	0.20
HYBRID	8.66	4.00	8.62	4.00	5.46	4.53
ARE	47.09	27.93	46.95	27.93	20.68	27.83
EABS	0.80	1.06	0.80	1.06	1.31	0.99
SNE	5.81	4.07	**3.34**	4.07	4.21	4.61
Redlich-Peterson						
K_R (l/g)	0.11	0.09	0.11	0.09	0.09	0.10
a_R (l/mg)	0.07	0.04	0.07	0.04	0.02	0.03
g	0.99	1.09	0.99	1.09	1.22	1.16
R²	0.99	0.99	0.99	0.99	0.98	0.98
Chi test	0.04	0.03	0.04	0.03	0.16	0.04
ERRSQ	0.02	0.02	0.02	0.02	0.05	0.03
HYBRID	0.75	0.57	0.75	0.57	3.14	0.75
ARE	9.43	6.88	9.65	6.88	6.31	7.28
EABS	0.30	0.35	0.36	0.35	0.95	0.32
SNE	5.98	5.09	**3.62**	5.09	4.76	5.60

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