Investigation of the Adsorption Potentials of an Organic Adsorbent for Phenol Removal from Aqueous Solution

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Authors' contributions

This work was carried out in collaboration among all authors. Author CEMO designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Author IAOO managed the analyses of the study and author JNN managed the literature searches. All authors read and approved the final manuscript.

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ABSTRACT

Phenol is a prevalent pollutant found in many industrial wastewaters, and it is paid singular attention because of its special features including high toxicity, carcinogenic properties, and vital cumulative ability that affects the health of humans and the environment. The current study investigated the removal of phenol from synthetic aqueous solutions using prepared *Moringa oleifera* seed shell as an adsorbent. The efficiency of phenol removal by *Moringa oleifera* seed shell was evaluated in a batch system, and different parameters such as initial concentration of phenol (100, 200, 300, 400 and 500 mg/L), contact time (10, 20, 30, 40, 50 and 60 min), and adsorbent dosage (0.2, 0.4, 0.6, 0.8, and 1.0 g) were studied. The results showed that the highest percentage of phenol removal by the ash occurred at 0.8 g dosage, contact time of 40 min, and initial concentration of 500 mg/L giving 87.2% phenol removal. The adsorption process was modeled with Langmuir and Freundlich isotherms and adsorption kinetics (pseudo-first order and pseudo-second order) at controlled temperatures. The results showed that the experimental data fitted the Langmuir (R^2 = 0.8338) much better than the Freundlich model (R^2 = 0.7314). For the

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analysis of the adsorption kinetics, the results showed that the experimental data fitted the pseudo-second order kinetics (R^2 = 0.999) much better than the pseudo-first order kinetics (R^2 = 0.5042). In general, the results of this study revealed that *Moringa oleifera* seed shell has suitable potential for use in removing phenol from aqueous solution on operation and practical scales due to its availability and organic nature.

Keywords: Adsorption; organic adsorbent; phenol; isotherm; kinetics.

1. INTRODUCTION

Wastewater refers to water that has been adversely affected in quality as a result of human or industrial activities which make it unsafe for usage in its current form [1]. The continuous discharge of organic pollutants such as phenol which are not degradable from effluents of manufacturing industries into water bodies has become a threat to the global community and thus posing a serious threat to the survival of life. In order to protect the environment from the hazardous effects associated with phenolic wastewater discharge, proper treatment methods that can effectively remove or reduce the contaminants present in the wastewater [2]. These treatment methods for water purification involves the removal of undesirable chemical compounds, biological contaminants, suspended solids and gases present in the contaminated water. Some of these treatment methods are adsorption, ion exchange, reverse osmosis, chemical oxidation, precipitation, distillation, solvent extraction and bio-remediation.

Adsorption process has been established to be the most effective method for the removal of colour, phenol, odour, organic and inorganic pollutants from wastewater due to its ability to accumulate the gas or liquid solute on the surface of a solid or liquid through formation of film of molecules or atoms called adsorbate [3]. Owing to its versatility and ease of operation, it is one of the most commonly used waste water treatment methods for removal of phenols and phenolic compounds.

Phenol is also known as carbolic acid which belongs to a carboxyl and alcohol group, the molecular formula is C_6H_5OH and it is an organic compound with physical and chemical properties as shown in Table 1. Phenol is a benzene derivative and is the simplest member of the phenolic chemical [4]. The molecule consists of a phenyl ($-C_6H_5$) bonded to a hydroxyl (-OH) group then having its chemical formula as C_6H_5OH.

Phenol is considered as the main pollutant of concern because of the harmful and toxic effect, which can be accumulated in living organism. Due to the concern, the level of phenol in drinking water and effluent has been also limited by international act and each country has proposed many profitable and non-profitable agencies such as Environmental Protection Agency (EPA), and World Health Organization (WHO) established. Phenol exposure either directly or accidently can disrupt the metabolic system in microorganism, human or animal. Phenol can enter living organism through three different routes: dermal contact, ingestion, and inhalation. According to Health Protection Agency (HPA), 2007, phenol effluent standards from different industrial discharges have been set as shown in Table 2.

Table 1. Physical properties and chemical identity of phenol

Properties	Data
Melting point, ^0C	43
Boiling point	181.8
Vapour pressure, at 25^0C	0.3513
Density, at 20^0C relative to density of H_2O at 4^0C	1.0567
Flash point (open cup)	85^oC
Water solubility, g/L at 25^0C	87
Odour threshold	0.447 ppm (0.18 mg/m^3)- 100$^0/_0$ response 0.006 ppm (0.02 mg/m^3)- sensitive.
Molecular weight	94.2 g/gmol
Phenol solution	Colourless.

Table 2. Phenol effluent standards from different industries

S/n	Type of industry	Discharge limit
1	Coal washers (Phenolic)	1.0 mg/L
2	Coke oven (Phenolic as $C_6H_5OH_)$	5 mg/L
3	Dye & dye intermediate industry (Phenolic as C_6H_5OH)	1.0 mg/L
4	Integrated iron & Steel plant	1.0 mg/L
5	Cotton textile industry	5.0 mg/L
6	Oil refinery	0.35 mg/L
7	Oil drilling & Gas extraction Industry	1.2 mg/L
8	Organic chemicals manufacturing Industry	5 mg/L
9	Paint industry	1.0 mg/L
10	Pesticide industry	1.0 mg/L
11	Petrochemicals	5.0 mg/L
12	Pharmaceuticals industry	1.0 mg/L
13	Small scale industry	5.0 mg/L

The aim of the present work is to investigate *Moringa oleifera* seed shell as a potential adsorbent for phenols removal from aqueous solution. In details, characterization of the organic precursor and factor interaction studies using batch adsorption medium was performed to establish the optimum process conditions. In addition, the equilibrium isotherm models: Langmuir and Freundlich models and equilibrium kinetics models: pseudo-first order and pseudo-second order were determined using the experimental data.

2. MATERIALS AND METHODS

2.1 Preparing Phenol Solution

Phenol used is of analytical grade manufactured by Merck Company and was purchased from the local market in Enugu city, Nigeria. Stock solutions of phenol were prepared by dissolving 1000 mg of 2,4,5-trichlorophenol (99.9% purity) in 1 L of distilled water without pH adjustment. Working solutions of the desired concentrations (100, 200, 300, 400 and 500 mg/L) were obtained by successive dilutions.

2.2 Calibration Curve Analysis

Ultraviolet-visible spectrophotometer (Shimadzu, Model UV - 1800) was used to measure the phenol concentration. To establish a reference wavelength for its measurements, a base line correction is carried out by filling both the cuvettes with the blank solution and using the option of base line correction on the spectrophotometer. The phenol solution is then placed into the sample cuvette to get a graph of the ultraviolet absorption of the solution over the range of wavelengths. The maximum wavelength, $λ_{max}$ = 276 nm was obtained showing the value at the peak which gives the wavelength of maximum absorption for the given concentration of phenol. The calibration plot for the desired phenol concentrations is shown in Table 3 and its corresponding plot is shown in Fig. 1.

2.3 Adsorbent Preparation

Matured pods of *Moringa oleifera* were purchased from the local market of Enugu city, Nigeria. The seeds were removed from the pod and dried under the sun at about 35°C for 3 days. The external shells were removed; washed with distilled water to remove impurity such as sand, leaves, soluble and colored components; dried at 50°C for 8 hr; crushed in a domestic grinder and sieved to obtain particle sizes in the range of 0.6 mm – 1 mm. Then, 20 g of the powdered adsorbent (*Moringa oleifera* seed shell), was soaked in 100 mL of 0.5 M HCl overnight. The chemically activated adsorbent was filtered, washed with distilled water and dried in the thermostatic oven at 100°C. The activated adsorbent was then used in adsorption experiments.

Table 3. Calibration of phenol solution

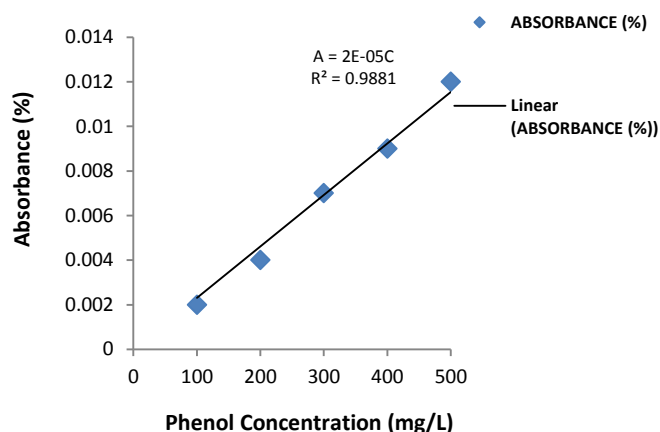| Concentrations of Phenol (mg/L)	Absorbance (%)
100	0.002
200	0.005
300	0.007
400	0.009
500	0.012

Fig. 1. Calibration plot for Phenol Concentration

2.4 Batch Adsorption Experiments

Batch adsorption experiment were conducted in order to determine the optimum conditions favourable for the adsorption process and also to generate adsorption isotherm and adsorption kinetics data. In the batch adsorption study, a measured amount of the activated adsorbent (0.2 – 1.0 g) was placed in a 250 mL beaker containing 50 mL of desired phenol concentration (100 – 500 mg/L). In order to maintain the pH of the suspension, buffer with a pH of 6 was prepared by diluting the buffer tablet/powder in 100 mL distilled water and adjusting it using 1 M HCl and 1 M NaOH. 20 mL of the prepared pH was added to the suspension. The sample was stirred using a magnetite stirrer for 20 min at 100 rpm. After the desired contact time, the sample was filtered through Whatman-42 filter paper and the concentration of phenol in the filtrates was analyzed using UV-Vis Spectrophotometer. All experiments were performed at room temperature, 30 ± 2°C and in duplicate. Final results are reported as the average of the two measurements. The phenol removal efficiency was calculated using:

$$\text{Phenol Removal \%} = \frac{(C_0 - C_t)}{C_o} \; x \; 100 \qquad (1)$$

where C_o and C_t are the initial and final adsorbate concentrations in solution (mg/L). The equilibrium phenol adsorbed, q_e and the amount of phenol adsorbed per time, q_t is giving as:

$$q_e = V \frac{(C_0 - C_e)}{M} \qquad (2)$$

$$q_t = V \frac{(C_o - C_t)}{M} \qquad (3)$$

where C_e is the equilibrium concentrations in solution, V is a known volume of the synthetic wastewater (L), and M is a known mass of dry adsorbent (g).

2.4.1 The effect of adsorbent dosage

The effect of adsorbent dosages on the removal of phenol from the solution was carried out. Adsorbent dose was done in a range of 0.2 to 1.0 g per 50 mL of a solution containing 400 mg/L phenol at pH 6 and contact time of 40 min.

Samples was stirred using magnetic stirrer, at the elapsed time, it was filtered and analyzed.

2.4.2 The effect of contact time

To measure the effect of contact time on adsorption process, tests were done at different times (10, 20, 30, 40, 50 and 60 min) for the primary phenol concentration of 400 mg/L at pH = 6 and 30 ± 2 ℃. 0.8 g of adsorbent dosage was dissolved in 50 mL water in a 250 mL beaker and the samples was stirred using magnetic stirrer, at the elapsed time, it was filtered as mentioned earlier and analyzed.

2.4.3 The effect of initial phenol concentration

In this stage 0.8 g of adsorbent is dissolved in 50 mL of water. This quantity was used for different phenol concentrations (100, 200, 300, 400, and 500 mg/L) at pH of 6 and contact time

of 50 min. Then, the samples were filtered and analyzed as mentioned before.

3. RESULTS AND DISCUSSION

3.1 Proximate Analysis

The proximate analysis shows a high fiber content suitable to adsorb phenols onto the adsorbent pores as shown in Table 4. Fibre content present established the precursor as an organic polymer with repeating small molecules that could extend as tails and loops when dispersed in water [5]. The moisture content value shows the hydrophilic nature of the adsorbent. The presence of fibre and moisture justified the use of the precursor as an adsorbent in this work.

Table 4. Proximate analysis of *Moringa oleifera* seed shell

Content	Weight %
Moisture	9.799
Ash	18.076
Fiber	3.825
Fat	0.549
Protein	6.30
Carbohydrate	61.451

3.2 FTIR Analysis

Fourier transform infrared spectrophotometer was used to scan the adsorbent at a wavelength of 600 – 4000 cm^{-1} to obtain its spectra heights as shown in Fig. 2. The high intensity and sharp peaks observed in the adsorbent may be due to the highly crystalline nature of the products. The broad adsorption bands (cm^{-1}) at 3314.39379 cm^{-1} and 3104.92445 cm^{-1} may be assigned to the –OH and –COOH stretching vibrations [6]. Specific olefinic vibrations may be the cause of the band at 1612 cm^{-1} and the skeletal C vibrations in aromatic rings bands in the 1600–1400 cm^{-1} region of the spectrum. Absorption due to C–O vibrations occurs between 1300 and 850 cm^{-1}. The band at 1265 cm^{-1} may be due to esters and the strong one at 1046 cm^{-1} to C–O vibration in C–OH (5). Only bands attributed to aromatic C=C and C–O vibrations absorbing between 1439 and 850 cm^{-1} and a band at 767 cm^{-1} due to aromatic C–H vibrations are clearly displayed in the spectra of *Moringa oleifera* seed shell. The spectra of the *Moringa oleifera* seed shell contains principally the bands associated to the C=C, C-O and C–H aromatic vibrations between 1437 and 767 cm^{-1}.

3.3 Effect of Adsorbent Dosage on the Phenol Removal

The adsorptive capacity of the adsorbent is one of the most important parameter for determining the initial phenol concentration. In Fig. 3, phenol removal depends on dosage in solution and will increase with increasing adsorbent dosage. It
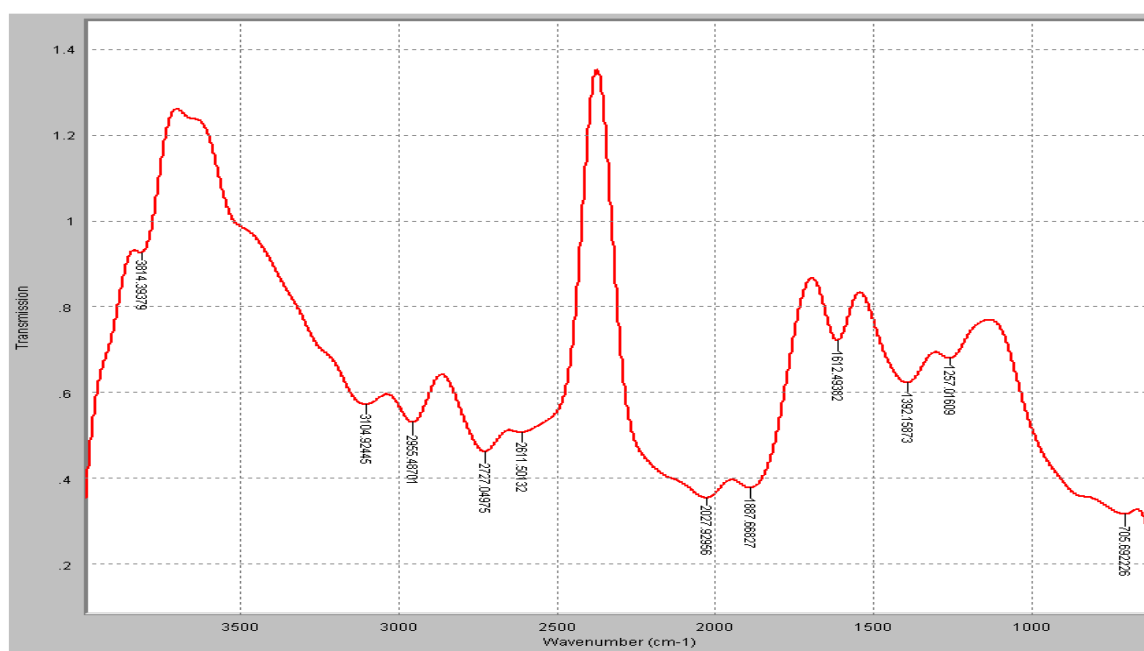

Fig. 2. FTIR spectra of *Moringa oleifera* seed shell

shows that the percent phenol removal increased with increasing adsorbent dosage up to 0.8 g, having the maximum removal efficiency of 60.0 %. It would seem that there will be areas on the adsorbent surface remained unsaturated during the adsorption process but the adsorption locations could be increased by increasing the adsorbent dosage. The graph shows a reversal on the efficiency after 0.8 g showing the attainment of the highest rate of adsorption. This clearly indicates the saturation of the adsorption sites of the adsorbent.

3.4 The Effect of Contact Time on the Phenol Removal

Fig. 4 shows the effect of exposure time on the phenol concentration and the percentage of phenol elimination in primary phenol concentration of 500 mg/L. The phenol concentration decreases significantly at the first stages of adsorption and reached equilibrium after 50 min with the maximum removal efficiency of 87.2%. This shows that the phenol removal rate of adsorption was rapid at the onset but the rate reduced until the equilibrium sets in. It could be further explained that at the initial stage of adsorption the numbers of free spaces available on the adsorbent surface are more, and then due to the repulsion force between the adsorptive molecules and the remained free surface of soluble phase after some times, adsorption becomes slower and harder.

3.5 The Effect of Adsorbent Dosage and Contact Time on Adsorption Capacity

The Effect of adsorbent dosage and contact time on adsorption capacity is shown in Figs. 5 and 6, having the maximum adsorption capacities of 34.125 mg/g and 38.15 mg/g respectively. Although, the elimination rate of phenol will be increased with increasing dose of adsorbent, but the amount of adsorbed phenol for each gram of adsorbent will be decreased, because phenol concentration in the solution (500 mg/L) will be decreased due to adsorption by activated unsaturated areas of adsorbent surface and increasing adsorption also causes aggregation of particles. As the surface adsorption sites become exhausted, the rate of uptake is controlled by the rate of transport from the exterior to the interior sites of the adsorbent particles.

3.6 Adsorption Isotherms

Studying of isotherms could explain the reactions between adsorbent and adsorption. Isotherm shows the relation between soluble phenol concentration and the rate of absorbed phenol by the solid phase, when the two phase are in balance. The Langmuir isotherm relates the adsorption of molecules on a solid surface to concentration of a medium above the solid surface at a fixed temperature [7]. Once the adsorbate attaches onto a site, no further adsorption can take place at that site and therefore the adsorption process is monolayer in nature. The linear form of the Langmuir equation is:

$$\frac{C_e}{q_e} = \frac{1}{q_o K_L} + \frac{C_e}{q_o} \qquad (4)$$

Where C_e (mg/L) is the equilibrium concentration of phenol, q_e (mg/g) is the amount of phenol adsorbed per unit mass of adsorbent, and q_o (mg/g) and K_L (L/mg) are Langmuir constants related to adsorption capacity and rate of adsorption respectively. A graph of C_e/q_e versus C_e would give a straight line having a slope of $1/q_o$ and intercept of $1/q_o K_L$.

The Freundlich model is an empirical equation based on adsorption onto a heterogeneous surface supporting sites of varied affinities [8]. It is assumed that stronger binding sites are occupied first and that the binding strength decreases with the increasing degree of site occupation. The linear form of the Freundlich equation is:

$$In q_e = In K_f + \frac{1}{n} In C_e \qquad (5)$$

Where K_f and n are Freundlich constants. A plot of ln q_e vs. ln C_e would give the values of the Freundlich constants K_f and $1/n$.

The plots of Fig. 7 and Fig. 8 show that the isotherm is of a monolayer adsorption with the correlation coefficient of 0.8338. The isotherm parameters are shown in Table 5.

Table 5. Isotherm parameters for phenol adsorption

Langmuir Isotherm			Freundlich Isotherm		
q_o(mg/g)	K_L(L/mg)	R_L^2	K_f mg/g (L/mg)$^{1/n}$)	n	R_f^2
54	0.0318	0.8338	5.623×10^{14}	0.1675	0.7314

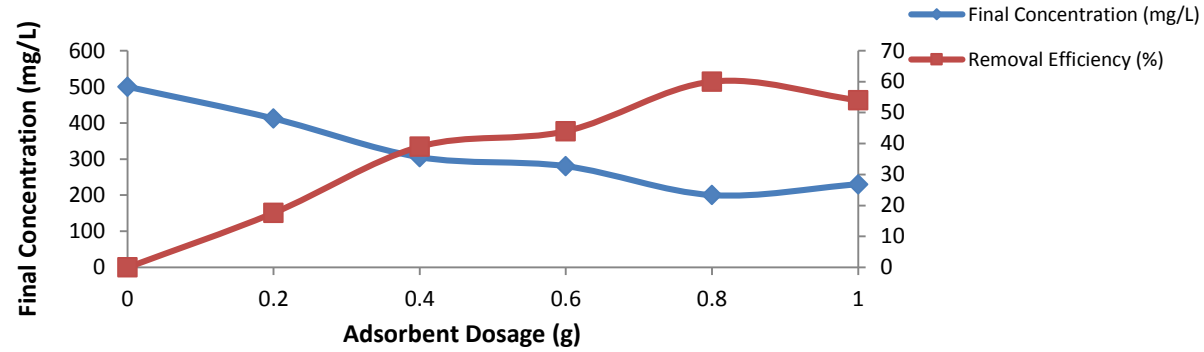**Fig. 3. Effect of adsorbent dosage on the adsorption of phenol onto activated carbon (Phenol concentration = 500 mg/L; pH= 6; Contact time = 40 min)**
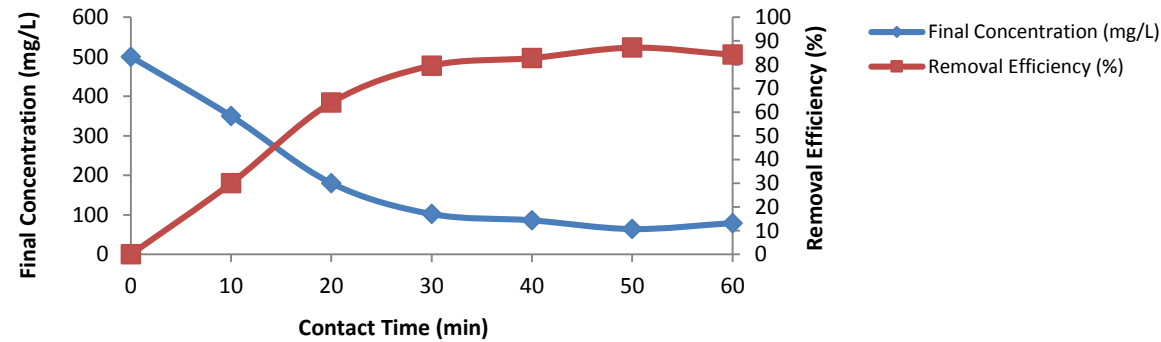

Fig. 4. Effect of contact time on the adsorption of phenol (Phenol concentration: 500 mg/L, pH: 6, adsorbent dosage: 0.8 g)
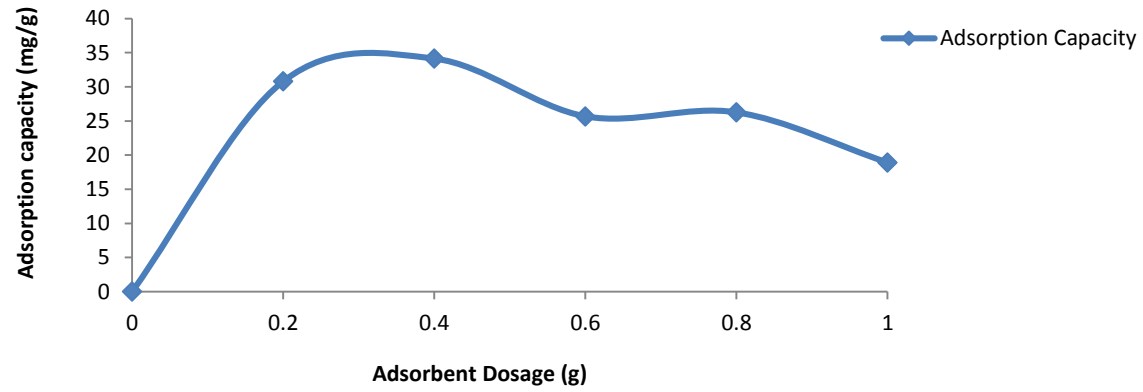
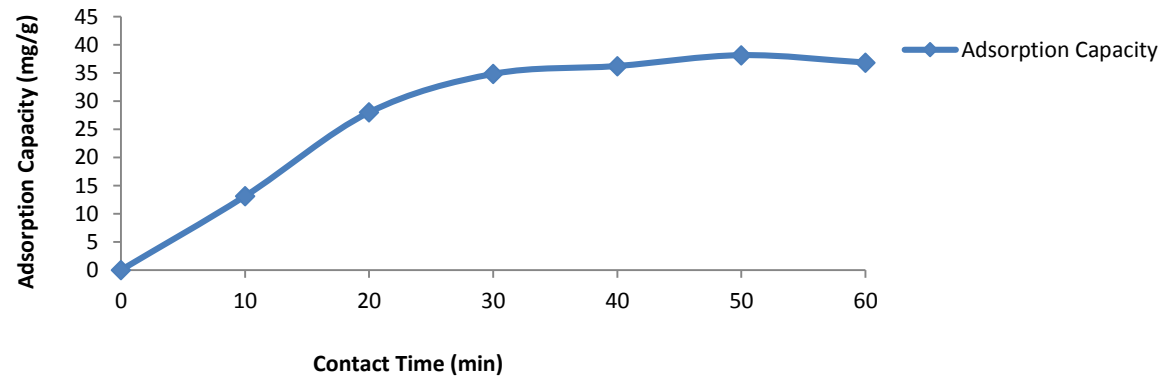**Fig. 5. Effect of adsorbent dosage on adsorption capacity**

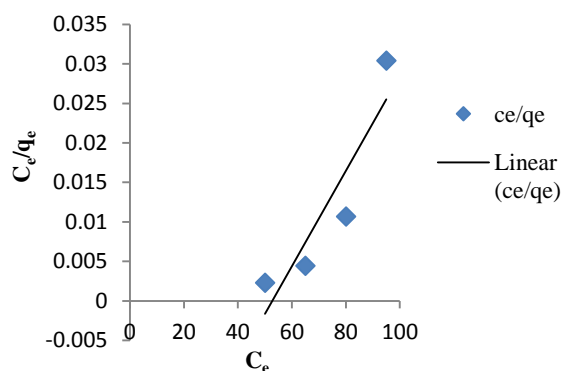**Fig. 6. Effect of contact time on adsorption capacity**

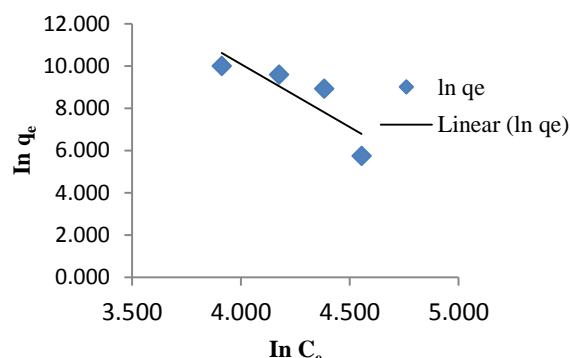**Fig. 7. Plot of Langmuir Isotherm**

Fig. 8. Plot of Freundlich Isotherm

3.7 Adsorption kinetics

The prediction of the adsorption rate gives important information for designing batch adsorption systems [5]. Kinetics is an adsorption dynamic which describes the solute uptake rate and evidently control the resident time of adsorbate and possibilities of desorption [9]. The Lagergren rate equation is one of the most widely used sorption rate equations for the adsorption of a solute from a liquid solution [10]. The pseudo-first-order equation is given as:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{6}$$

Where q_t is the amount of adsorbate adsorbed at time t (mg/g), q_e is the adsorption capacity at equilibrium (mg/g), K_1 is the pseudo first order rate constant (min^{-1}), and t is the contact time (min). The integration of the above equation with for the boundary conditions; t = 0 to t = t and q_t = 0 to q_t= q_t, gives:

$$\log(q_e - q_t) = \log q_e - \left(\frac{K_1}{2.303}\right)t \tag{7}$$

The values of adsorption rate constant (K_1) for phenol adsorption on *Moringa* oleifera seed shell will be determined from the plot of log (q_e - q_t) against t. The pseudo-second-order model is given as:

$$\left(\frac{dq_t}{dt}\right) = K_2(q_e - q_t)^2 \tag{8}$$

Where K_2 is the pseudo-second-order rate constant (g/mg.min), q_e is the amount of phenol adsorbed at equilibrium (mg/g), and q_t is the amount of phenol adsorbed at time t (mg/g).

Integrating for the boundary conditions t = 0 to $t = t$ and q_t=0 to q_t = q_t gives

$$q_t = \frac{q_e^2 K_2 t}{1 + q_e K_2 t} \tag{9}$$

Eq. (9) is the integrated rate law for a second order reaction and can be rearranged to obtain

$$q_t = \frac{t}{\frac{1}{K_2 q_e^2} + \frac{t}{q_e}} \tag{10}$$

The initial adsorption rate, *h* (mg/g.min) is defined as:

$$h = K_2 q_e^2 \tag{11}$$

The rate parameters k_2 and q_e can be directly obtained from the intercept and slope of the plot (t/q_t) against t. Study on the kinetic models as shown in Figs. 9 and 10 shows that the adsorption kinetics of *Moringa oleifera* seed shell fits best to pseudo-second order kinetics having R^2 value of 0.999 as compared to the pseudo-first order kinetics with R^2 value of 0.504. This indicates that the adsorption is more inclined to chemisorption [10-12].

Table 6. Adsorption kinetics parameters

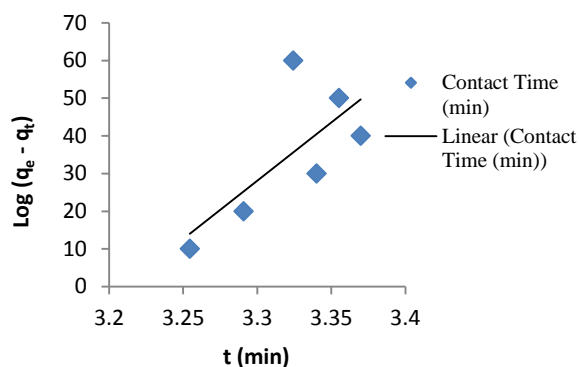| Pseudo-first Order			Pseudo-second Order		
K_1 (min^1)	q_e (mg/g)	R^2	K_2 (g/mg min)	q_e (mg/g)	R^2
0.007	1.361	0.504	0.173	25	0.999

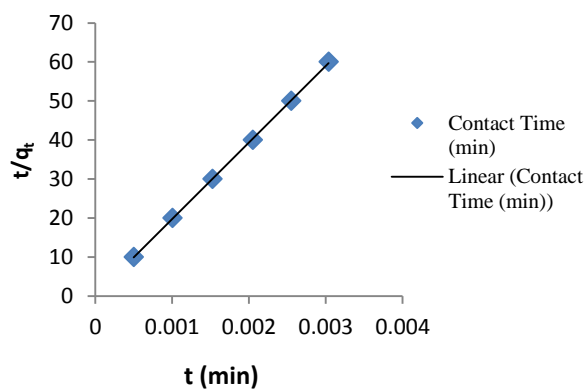**Fig. 9. Pseudo first-order kinetics model Fig. model**

Fig. 10. Pseudo-second order kinetics

4. CONCLUSION

In this study it is clearly observed that *Moringa oleifera* seed shell can be used effectively for the removal of phenol from aqueous solutions. Removal rate of phenol depends on amount of adsorbent dosage, contact time, and initial concentration of phenol. *Moringa oleifera* seed shell can remove more than 87.2% of phenol from aqueous solutions with an initial phenol concentration of 500 mg/L. Phenol adsorption model result shows the agreement of Langmuir adsorption isotherm with favourable R^2 value of 0.8338, indicating that the adsorbent is monolayer in nature. The kinetic models show that the adsorption rate data followed the pseudo-second order kinetics with R^2 value of 0.999. This is a clear indication that the adsorption is more inclined to chemisorption mechanism. In conclusion, the use of low cost adsorbent like *Moringa oleifera* seed shell may contribute to the sustainability of the environment.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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